

Advances in Polymer Science

93

M. L. Fridman, V. D. Sevruk
Extension of Molten Polymers

M. L. Fridman, S. L. Peshkovsky
Molding of Polymers under Conditions of
Vibration Effects

M. L. Fridman, A. Z. Petrosyan, V. S. Levin,
E. Y. Bormashenko
Fundamentals of Low-Pressure
Molding of Polymer Pastes (Plastisols) and
Thermoplastic Materials

V. I. Tunkel, M. L. Fridman
Granulated Thermosetting Materials
(Aminoplasts) – Technology

Polymer Processing



Springer-Verlag

Polymer Processing

Editor: M. L. Fridman

With contributions by

E. Yu. Bormashenko, M. L. Fridman, V. S. Levin,
S. L. Peshkovsky, A. Z. Petrosyan, V. D. Sevruck,
V. I. Tunkel

With 80 Figures and 13 Tables



Springer-Verlag Berlin Heidelberg New York
London Paris Tokyo Hong Kong

ISBN-3-540-51376-0 Springer-Verlag Berlin Heidelberg New York
ISBN-0-387-51376-0 Springer-Verlag New York Berlin Heidelberg

Library of Congress Catalog Card Number 61-642

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in other ways, and storage in data banks. Duplication of this publication or parts thereof is only permitted under the provisions of the German Copyright Law of September 9, 1965, in its version of June 24, 1985, and a copyright fee must always be paid. Violations fall under the prosecution act of the German Copyright Law.

© Springer-Verlag Berlin Heidelberg 1990
Printed in Germany

The use of registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Bookbinding: Lüderitz & Bauer, Berlin
2152/3020-543210 — Printed on acid-free paper

Editors

- Prof. Henri Benoit, CNRS, Centre de Recherches sur les Macromolécules, 6, rue Boussingault, 67083 Strasbourg Cedex, France
- Prof. Hans-Joachim Cantow, Institut für Makromolekulare Chemie der Universität, Stefan-Meier-Str. 31, 7800 Freiburg i. Br., FRG
- Prof. Karel Dušek, Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 16206 Prague 616, ČSSR
- Prof. Hiroshi Fujita, 35 Shimotakedono-cho, Shichiku, Kita-ku, Kyoto 603, Japan
- Prof. Gisela Henrici-Olivé, 1332 Neal Road, Cantonment, Florida 32533, U.S.A.
- Prof. Dr. habil. Günter Heublein, Sektion Chemie, Friedrich-Schiller-Universität, Humboldtstraße 10, 69 Jena, DDR
- Prof. Dr. Hartwig Höcker, Deutsches Wollforschungsinstitut e. V. an der Technischen Hochschule Aachen, Veltmanplatz 8, 5100 Aachen, FRG
- Prof. Hans-Henning Kausch, Laboratoire de Polymères, Ecole Polytechnique Fédérale de Lausanne, 32, ch. de Bellerive, 1007 Lausanne, Switzerland
- Prof. Joseph P. Kennedy, Institute of Polymer Science. The University of Akron, Akron, Ohio 44325, U.S.A.
- Prof. Anthony Ledwith, Pilkington Brothers plc, R&D Laboratories, Lathom Ormskirk, Lancashire L40 5UF, U.K.
- Prof. Seizo Okamura, No. 24, Minamigoshi-Machi Okazaki, Sakyo-Ku, Kyoto 606, Japan
- Prof. Salvador Olivé, 1332 Neal Road, Cantonment, Florida 32533, U.S.A.
- Prof. Charles G. Overberger, Department of Chemistry. The University of Michigan, Ann Arbor, Michigan 48109, U.S.A.
- Prof. Helmut Ringsdorf, Institut für Organische Chemie, Johannes-Gutenberg-Universität, J.-J.-Becher Weg 18-20, 6500 Mainz, FRG
- Prof. Takeo Saegusa, Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto, Japan
- Prof. John L. Schrag, University of Wisconsin, Department of Chemistry, 1101 University Avenue, Madison, Wisconsin 53706, U.S.A.
- Prof. William P. Slichter, Executive, Director, Research-Materials Science and Engineering Division AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, NJ 07974, U.S.A.
- Prof. John K. Stille, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, U.S.A.

Editor's Foreword

Processing of polymers is one of the most important and rapidly progressing industries the theoretical basis of which is gaining respect. Plastic processing technology and the development of the relevant equipment can not be considered today merely as a set of empirical approaches employed to manufacture high-quality products. Such approaches would mean a "retreat" and a reduction of activities in this field to mediocrity and enclose the process within the framework of just an accumulation of skills and knowledge about "standard" cases of manufacturing experience.

The fact is that, in the long history of polymer processing, engineering and design has always been ahead of theory. The development of screwless (or disc-type) extruders, innovative for their time, on the basis of the earlier-discovered normal stress effect (which received the name of the Weissenberg effect) was, apparently, one of the few exclusions. However, this example has clearly demonstrated the potential and the role of theoretical research in the progress of technology.

The situation in the field of processing has been changing during recent years. A number of research projects have contributed to the development of theoretical premises not only for the intensification and optimization of the known processes but also for development of new technologies and products. This can be easily exemplified: successful studies of the orientation crystallization of polymers have provided a basis for the commercial production of superstrong materials (fibers, films, etc.); data on changes in the structure and mechanical properties of polymers under extrusion have been used to develop the technology and equipment for manufacturing of film threads and fibers (including the fibrillated ones); development of the composite shear theory and demonstration of the possibility of reducing the viscosity of melts and intensifying their flow when the polymer is in the combined-stress state occurring at low- and high-frequency oscillations (vibrations) of the molding tool have stimulated the search for designs of machinery with an increased molding rate attained on the basis of the above mentioned effect; development of mathematical models of many operations and processes, generally, has become an inalienable part of the automatization and computerization

of the modern production lines; finally, the theory has provided a reliable basis for computer-aided engineering of the main working elements of extruders, casting machines, extrusion heads, and molding tools.

The list of similar achievements could easily be extended but even the above cited examples are sufficient to conclude that the further progress of polymer processing depends strongly on the successful development and improvement of the theoretical basis of technology. We hope that this publication will make a practical contribution to the elimination of the still-existing gap between "science" and "technology".

Certainly, it is impossible to review all the new developments in polymer processing in one book even if we limit ourselves to the short period of the last 5–10 years. This, however, had been planned neither by the publisher nor by the editor. We have collected under one cover four reviews every one of which, we believe, illustrates different routes of the progress of scientific knowledge in the sphere of polymer processing and demonstrates various stages in the development of this knowledge and its practical application.

Thus the review on the problem of molten polymer extension (M. L. Fridman & V. D. Sevruk) describes not only achievements of the theory and experiments but also new approaches to estimation of the quality of thermoplastics on the basis of melt extension tests under constant-force conditions. During the next few years we may expect development of new instrumentation and standard procedures for testing raw materials used to manufacture films, fibres, etc. In other words, these data are available for practical application and it is high time we took advantage of them.

Another review on the problem of polymer molding under vibration effects is, in our view, fundamentally important. The idea of this publication is not only to analyze and generalize results of combined-shear studies but also to attract attention of experts to the two latest achievements: theoretical and experimental corroboration of the efficiency of physical effects upon molten polymers in molding processes, and discovery of a new phenomenon — acoustic cavitation of molten polymers — which had not been predicted by the cavitation theory for fluids with a viscosity that high. Practical applications of this effect in manufacturing technologies have still to be developed. However it is clear right now that it has a high potential, since the melt cavitation conditions permit us to adjust the melt's rheological properties, to attain "dosed" mechanical destruction, excite active radicals in the polymer, disperse fillers, make new mixtures and alloys of polymers. We believe that the effect of acoustic cavitation opens a possibility of creating a new branch of plastic processing. However its present status leaves room for improvement: the effect has

been discovered and extensive scientific information is available, but it lacks the technology, or a number of technologies, which could be developed on that basis. We expect that these technologies will be characterized by low power consumption and high efficiency.

The situation is different in the case of processing of polymer materials at low pressure. Technology has been rapidly advancing in the sphere in recent years: centrifugal and rotary molding methods are widely used, the RIM-technology is generally accepted, polymer paste casting is used, etc. As regards the theory of the low pressure molding of polymer materials, it has not been completed so far and here we are facing again the situation when technology has leaped ahead of theory. We wished to demonstrate (M. L. Fridman, A. Z. Petrosyan, V. S. Levin, E. Yu. Bormashenko), using the example of a systematic review of the data on analysis and mathematical modelling of the casting of polymer pastes or plastisols, that science can provide a basis for automatization and optimization of the process, offer procedures for the analysis of optimum geometrical parameters of molding tools and temperature conditions of molding to be used by engineers and designers. An important point is that the developed approaches can be applied later to the analysis of the molding of low-viscous thermoplastics and other low-pressure processing technologies.

Finally, we suppose that the review on the aminoplastic granulation technology (V. I. Tunkel, M. L. Fridman) illustrates another level of the development of processing. The analysis makes it clear that the situation in this case is quite the opposite: a scientific basis of the granulation process is available but the optimum engineering solutions are still to be found. Therefore we have focused on the comparative analysis of machinery and equipment for the process. It should be noted that although aminoplastic nodulizing technology has been practically abandoned during recent years, the interest for this technology can be reanimated, apparently, due to the new engineering approaches.

Certainly, the above mentioned does not give a full answer to the question, why these four articles have been included into this collection. It is natural that they have been selected primarily with regard to the scientific and engineering interests of the editor (who is also one of the authors) and include works carried out during recent years together with junior colleagues.

In conclusion I wish to express my gratitude to Springer Verlag and, personally, to the Chemistry Editor Dr. R. Stumpe for granting us the opportunity to use a special issue of this much respected journal to disseminate our knowledge.

Moscow, October 1989

Professor M. Fridman

Table of Contents

Extension of Molten Polymers M. L. Fridman, V. D. Sevrak	1
Molding of Polymers under Conditions of Vibration Effects M. L. Fridman, S. L. Peshkovsky	41
Fundamentals of Low-Pressure Molding of Polymer Pastes (Plastisols) and Thermoplastic Materials M. L. Fridman, A. Z. Petrosyan, V. S. Levin, E. Yu. Bormashenko	81
Granulated Thermosetting Materials (Aminoplasts) — Technology V. I. Tunkel, M. L. Fridman	137
Author Index Volumes 1–93	175
Subject Index	189

Extension of Molten Polymers

M. L. Fridman, V. D. Sevruck

USSR Research Institute of Plastic Materials

Perovsky pr. 35, Moskow 111 112, USSR

This contribution reviews the major results of studies of the extension of molten polymers which have been carried out recently. The authors discuss systematically basic regularities of the extension of molten polydisperse polymers including the uniform extension and its development in time (at a constant strain velocity and at constant extrusion force). The article also considers the dependency of stress and strain velocity upon elastic strain, stress and strain relaxation processes; the major differences in the variations of effective viscosity under extension are pointed out. The authors describe the effect of polymer fluid flow retardation under high elastic strains.

The article reviews the latest achievements in the sphere of theoretical descriptions of the molten polydisperse polymers and gives various molecular-kinetic models of extension.

Also described are some important technological applications in the processing of polymers, including the methods of examination and verification of the properties of raw materials by means of tests in which molten polymers are extended at a constant force, and molding of sleeve-type and flat films.

The analysis has corroborated that the extension experiments were highly informative and important for science and technology.

1 Introduction	2
2 Major Regularities in Extension of Molten Polymers	4
2.1 Some Definitions	4
2.2 Homogeneous Extension of Polydisperse Polymers	6
2.2.1 General Aspects	6
2.2.2 Tensile Strain Development in Time. Extension at Constant Strain Velocity	7
2.2.3 Extension at Constant Force	8
2.2.4 Dependencies of Stress and Strain Velocities upon Elastic Strain	9
2.2.5 Stress and Strain Relaxation Processes	10
2.2.6 Some Differences in the Behavior of Effective Viscosity Under Extension	10
2.2.7 Retardation of Polymer Fluid Flow Under Great Elastic Strains	12
2.3 Theoretical Description of Extension in Molten Polydisperse Polymers	15
3 Extension of Molten Polymers and Molecular-Kinetic Theories	17
4 Some Technological Applications in Thermoplastic Processing	20
4.1 General Aspects	20
4.2 Study and Estimation of technological Properties of Polymers	21
4.3 Rheological Analysis of the Processes of Film Molding from Melts	32
4.3.1 Sleeve Films	32
4.3.2 Flat Film Canvas	33
5 References	38

1 Introduction

Practically all technologies of polymer processing are associated with extension of melts. In many cases it is an important but still "associate" effect as, for example, extension of melts in the zone close to the inlet to the molding part of extrusion heads, extension of jets during filling of molds in the course of pressurized casting. However, in a number of the major modern technologies of polymer processing the extension of melts is not an "effect" but the primary manufacturing operation principally critical for the process on the whole or, at least, for the production of special-purpose semifinished products and products with a present range of properties and geometrical dimensions. This group of processes includes, for example, molding of fibres, extrusion-inflated (sleeve) films with preset width and thickness, manufacturing of flat film blanks for production of thin and ultrathin uniaxially and biaxially oriented films, uniaxially oriented, flat threads ("refining") and fibrillated (splitted) elementary threads for further processing into twisted (braids, binder twines, ropes, etc.) and wattled items. The development of scientific fundamentals and improvement of the above-mentioned technologies requires a detailed knowledge and understanding of the behavior of molten polymers not only under shear strain (flow) but under tension, first of all at the outlet of the molding tools, which is usually called "spinneret drawing". It should be emphasized that the spinneret drawing in industrial technologies is complicated by a number of nontrivial rheological and physical/chemical phenomena, such as jet swelling at the outlet from the channel ("Barrus-effect"), nonisothermicity of flow and extension, development of chemical reactions under stress (thermomechanical destruction)¹⁾. We must admit that an understanding of these processes which could provide a basis for accurate and comprehensive calculations of the operation of molten polymer extension from molding tools has not been reached so far.

However, the applied importance of research into extension of melts is far from being limited by the above-mentioned aspects. Thus, for example, technological properties of polymers, mixtures, and compositions based thereon have been so far classified and compared primarily in terms of rheological (first of all viscous) properties of melts under shear strain conditions which is not only "poor" from the point of view of information but is absolutely noncharacteristic of cases when, as mentioned above, the principally important technological stage is not the shear flow but extension (jet drawing). Development of another approach to analysis of "adaptibility" and comparison of the properties of polymeric raw materials of different types (and even of different batches of polymers of one and the same brand) on the basis of extension tests of melts in recent years has become a problem of current concern for rheology, polymer-material study, and processing technology²⁾.

At first we have deliberately focused on the applied (technological) importance of the study of melt behavior under extension since the theoretical importance of the analysis of melt extension for polymer physics and mechanics can be regarded as already generally recognized. The scientific "success" and recognition of melt extension stems, we believe, from several fundamental causes, major of which are as follows. The geometrical pattern of deformation (shear, twisting, tension, etc.) is not very important for mechanics of the usual solid bodies since there is a well-known and multiply verified connection (linear Hooke's mechanics) between the main (if

not been all) characteristics. It also holds true, on the whole, in case of a purely viscous fluid: shear flows in such media (Newton's law) are of major interest from the practical point of view, and viscosity under tension equals triple shear viscosity (Trutone's principle) and these laws characterize sufficiently the behavior of molten polymers in the linear strain area^{3,4}. The situation is different in the area of their nonlinear behavior and the available characteristics of strain under shear do not necessarily permit to prognosticate the behavior of a material under extension. Therefore the study of regularities in the behavior of polymer fluids under extension is of general fundamental importance for construction of rheological models which describe and explain the behavior of these materials.

Another principal problem, beside the accumulation of significant reversible strains, which has stipulated theoretical and experimental interest in the discussed area of physics and mechanics of polymer fluids is the establishment of extension limits, i.e., to which extent polymer jets can be extended (ultimate, or rupture, extension rate). In reality the absolute limit (ultimate degree of extension of a macromolecular tangle when it turns into a stretched chain) is not reached, a jet breaks much earlier due to interslipping of macromolecules and the moment of rupture is determined by the strain velocity. A study of regularities in the accumulation of significant reversible strains has revealed (see, for example, Ref. ⁵) that there is a dependency of ultimate strains ϵ_e^* upon longitudinal strain velocity $\dot{\epsilon}$ given schematically in Fig. 1. At $\dot{\epsilon} \sim \dot{\epsilon}_f$ elastic strains, generally speaking, are low but complete critical strains (continuous curve in Fig. 1) are unlimitedly large since at $\dot{\epsilon} < \dot{\epsilon}_f$ plastic strains grow without increase in the elastic component (it relaxes completely and the polymer behaves as a usual viscous fluid). In this case the jet, certainly, is also destroyed but the mechanism of destruction is not the one specific for polymers. The situation alters after $\dot{\epsilon}_f$. At $\dot{\epsilon} > \dot{\epsilon}_f$, with increasing strain velocity (and, respectively, that of stresses), elastic strains grow and viscous flow strains drop. At $\dot{\epsilon} > \dot{\epsilon}_f$ the extension obligatorily results in a break (this has been proven clearly and comparatively long ago, for example, see Ref. ⁶), i.e., a steady flow can not be attained; point b in the diagram given in Fig. 1 corresponds to an approximate equality of reversible and irreversible strains; in the area of $\dot{\epsilon}_f < \dot{\epsilon} < \dot{\epsilon}_g$ the material being in the flow state is extended but after point b the elastic strains become increasingly dominating (although the flow is still noticeable) until, finally, at $\dot{\epsilon} > \dot{\epsilon}_g$ the flow can be practically neglected (polymer jet behaves like rubber), the extension is carried out under conditions of a forced high-elastic state and ϵ_e^* corresponds to rupture strain, the theoretical maximum of which is reached at point d at a certain velocity $\dot{\epsilon}_g$ sufficient for total

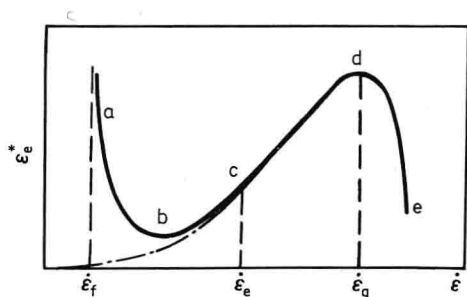


Fig. 1. Ultimate strains ϵ_e^* versus gradient of longitudinal velocity $\dot{\epsilon}$ in extension (explanations are given in the text)

straightening of the macromolecular tangle. The section d—e represent a strain of the polymer in which the higher the strain velocity, the lower relaxation effects and after point e they become practically completely suppressed just as if the polymer were glass.

Proceeding from the above-described pattern we can formulate two problems — different in physical sense and in equipment employed for implementation — in the manufacturing of oriented products ⁷⁾. The first one deals with attaining of maximum values of $\dot{\epsilon}_e^*$; this corresponds to implementation of such velocities and temperatures at which $\dot{\epsilon}$ approaches $\dot{\epsilon}_g$. Permissible strains are always limited here, flow does not take place, and there is a danger of breaking. This problem corresponds to modern high-speed processes of molding of chemical fibers (see, e.g., a recent review ⁸⁾ dealing with achievements in this field). The second problem is the attainment of very high extension degrees while maximum possible $\dot{\epsilon}_g^*$ are reached. The limit of this corresponds to strain velocity $\dot{\epsilon}_f$. A similar problem occurs in manufacturing of films by method of extrusion with sleeve inflation when it is required to extend (draw and inflate) the melt with the help of a circular spinneret so that the cross section of the blank was reduced by a factor of 20 to 50 (and even more) and to avoid the potential danger of sleeve breaking.

However this publication has been stipulated not only by the general theoretical and applied importance of the extension of polymer melts. A number of reviews dealing with these problems has been published recently (see, for example, Refs. ^{9,10)} These publications cover a sufficiently wide scope of literature. However, they fail, generally, to consider works on extension of polydisperse polymers carried out in the USSR as well as the achievements in the developing field of extension of monodisperse polymers. Note that mono- and polydisperse polymers differ significantly from one another in terms of rheological behavior, at least because of their different degrees of elastic strain: elastic strains in monodisperse polymers are very low, while elastic strains in polydisperse are gigantic.

We believe that it would be useful not only to generalize the latest achievements in the rheology of extension of mono- and polydisperse systems, but also to assume and analyze some specific technological applications. Earlier works, which have become almost “classical” are referred to only for chronological accuracy and completeness of the view.

2 Major Regularities in Extension of Molten Polymers

2.1 Some Definitions

Rheological experiments with molten polymers are normally arranged to investigate into the homogeneous inertialess extension under isothermal conditions.

Usually, investigations deal with uniaxial tension in a cylindrical sample which is easier to produce in experiments than other types of tension (see Fig. 2). In this case the strain velocity tensor is:

$$\mathbf{e} = \kappa \text{diag} \{1, -1/2, -1/2\} \quad (1)$$

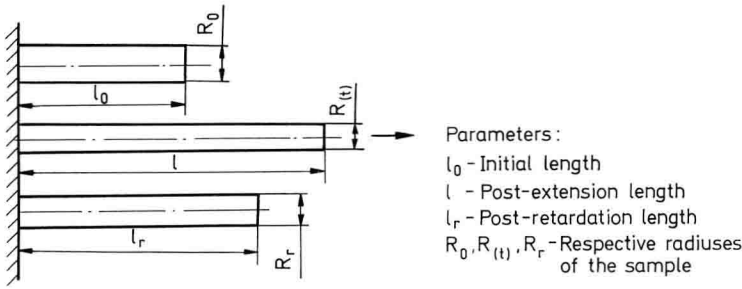


Fig. 2. Diagram of uniform extension and subsequent retardation of cylindrical polymer sample

In the cylindrical system of coordinates v, z, ϕ (axis z is directed along the sample) components of velocity are expressed as:

$$v_z = \kappa(t)z, \quad v_r = -\frac{\kappa(t)}{2} r, \quad v_\phi = 0 \quad (2)$$

If we neglect the effect of surface tension, there is only one component of stress tensor $\sigma = \sigma_{zz} = F/\pi R^2$ (F is extending force) independent of z in case of uniaxial tension of a cylinder.

Elongation is:

$$\varepsilon = l/l_0 = R_0^2/R^2 \quad (3)$$

where l_0 and R_0 are sample length and radius, respectively, at the starting moment of strain; l and R are length and radius at an arbitrary moment of extension (see Fig. 2). The second equality in Eq. (3) follows from the condition of the incompressibility of the media. According to the known dependency of total strain ε upon time t , the strain velocity κ is determined from the following formula:

$$\kappa = d(\ln \varepsilon)/dt \quad (4)$$

Longitudinal strain is taken as "elastic recoil":

$$\alpha = l/l_r = R_r^2/R^2 \quad (5)$$

or logarithm of this value. In Eq. (5) and l_r and R_r are, respectively, the length and the radius to which, at $t \rightarrow \infty$ (in experiments, this time is practically finite), tends an extended sample with length l and radius R after momentary lifting of tensile stress (see Fig. 2). Contraction occurs due to elastic energy accumulated in extension of the polymer fluid.

The value of irreversible longitudinal strain in experimental measurements is taken ^{11, 12} as:

$$\ln \beta = \ln \varepsilon - \ln \alpha, \quad \beta = l_p/l_0 \quad (6)$$

In this case the velocity of irreversible longitudinal strain can be determined in the following way:

$$\epsilon_p = d(\ln \beta) dt \quad (7)$$

Equation (7) was introduced in Refs. ^{13,14)} where its reasonability was proved when the expression was checked for correctness in the area of minor elastic strains.

2.2 Homogeneous Extension of Polydisperse Polymers

2.2.1 General Aspects

The very first experiments in extension of polymers in the viscous flow state ^{11,12,15)} demonstrated that $\sigma/\dot{\epsilon} \neq \text{const}$, as it is the case in Newtonian media. The relationship $\sigma/\epsilon_p = 3\eta$, true in the linear area under arbitrary conditions of tensile strain ^{13,14)}, does not hold true in the area of significant elastic deformations ^{11,12)}.

Later experimental research into extension was focused on detailed studies of the behavior of the medium's effective viscosity and the search for new effects under different conditions of extension.

Prior to a detailed discussion of the obtained experimental data we briefly list the major events — from our point of view — in chronological order.

1. *Ballman RL* ¹⁶⁾. Viscosity under stationary tension approaches the constant, while under shear at the same strain velocities it decreases rather intensively; unfortunately the experiment in extension was carried out within a limited range of strain velocities.

2. *Meissner Y* ^{17,18)}. Construction of dependencies $\sigma/\dot{\epsilon}$ versus time t (here σ is tension stress, $\dot{\epsilon}$ is strain velocity registered in the course of extension). The relationship $\sigma/\dot{\epsilon}$ (effective viscosity) being independent of $\dot{\epsilon}$ in the linear region, such a processing of experimental data allowed to separate reliably the regions of nonlinear strain; unfortunately this work failed to attain the stationary flow area (a principal matter for understanding of the rheology of such media), apparently, because of the limited capacity of instrumentation.

3. *Radushkevitch BV, Fichman VD, Vinogradov GV* ^{19,20)}. Stationary flow was attained under conditions of $\dot{\epsilon} = \text{const}$. Viscosity was increasing under stationary flow while the time during which the stationary flow was attained was reducing with increase in $\dot{\epsilon}$; unfortunately the experiment was carried out rather roughly and the authors failed to obtain clear dependencies of $\sigma/\dot{\epsilon}$ upon t ¹⁷⁾ therefrom.

4. *Munstedt H, Laun HM* ²¹⁾. Stationary flow was attained, which had not been revealed earlier in Refs. ^{17,18)} (the experiments were carried out with the same polymer). The time during which the stationary flow was attained and viscosity depending upon $\dot{\epsilon}$ passed via a maximum. The possibility of viscosity drop has been noted earlier in a work by Cogswell ²²⁾. The time during which the stationary flow was attained in the nonlinear area of flow ²¹⁾ could exceed significantly the relaxation time determined in the linear region.

5. *Prokunin AN* ^{23,24)}. Flow deceleration effect. Two maxima in dependencies of force upon time under conditions of $\dot{\epsilon} = \text{const}$ and respective flow deceleration (which

was judged from the velocity of irreversible strain). The time during which the second maximum was attained could exceed significantly the characteristic relaxation time determined from shear experiments in the linear area.

6. *Prokunin AN, Sevruk VD*²⁵⁾. Two polymers characterized by not much different flow curves can differ qualitatively at homogeneous extension under conditions $\kappa = \text{const}$ and $F = \text{const}$.

Let us discuss now in more detail the properties of polymers detected under homogeneous extension. We shall consider only two conditions: $\kappa = \text{const}$ and $F = \text{const}$ (as the two most characteristic examples of flow with preset kinematics and stress).

2.2.2 Tensile Strain Development in Time. Extension at Constant Strain Velocity

This type of extension has been studied experimentally in many works^{16-18, 21, 23, 26-33)}; data from Refs.^{18, 19, 24, 29, 31-33)} will be discussed in detail in subsequent sections.

Dependencies of stress σ and elastic deformation α upon time t are measured in extension under conditions of $\kappa = \text{const}$.

Let us consider the results of Refs.^{23, 26)}. The experiments were carried out with polyisobutylene (PIB) II-20 at 22 °C with molecular weight (MW) $\sim 10^5$, maximum Newtonian viscosity $\eta_0 = 1.1 \times 10^6 \text{ Pa} \cdot \text{s}$ and high-elasticity modulus $G_e = 1.57 \times 10^3 \text{ Pa}$; relaxation time was $\theta = \eta/G \sim 10^3 \text{ s}$. The constants were determined at shear.

Dependencies of dimensionless effective viscosity $\sigma/(\kappa\eta)$ upon time t under extension with constant strain velocity κ for different κ are given in Fig. 3. At low κ , when, at any t , the strain occurs in the linear region, the relationship $\sigma(t)/(\kappa\eta)$ does not depend upon κ (see the lower line in Fig. 3) and equals 3 under stationary flow. This dependency coincides in the linear region of deformation with effective viscosity at shear $[3\sigma_{12}/(\dot{\gamma}\eta)]$. With increase in κ , dependencies $\sigma/(\kappa\eta)$ coincide with the linear strain curve only in the beginning (minor elastic strains) and depart from it strictly increasing with further increase of t . At high values of t the flow may reach stationary conditions ($\sigma/\kappa = \text{const}$). The effective viscosity σ/κ and elastic strain α at stationary flow in the nonlinear strain region grow with increase of κ . Note also that the higher κ , the earlier in the the stationary flow is attained. In the linear strain region the time during which the stationary flow is attained is of the same order of magnitude as value θ .

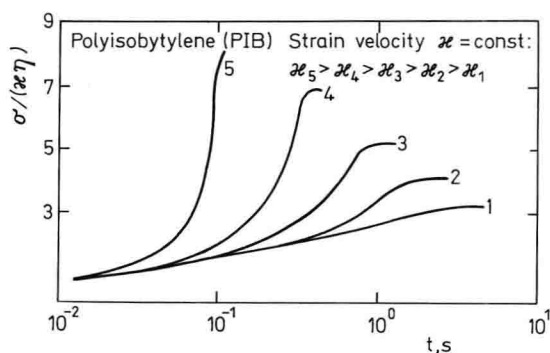


Fig. 3. Effective viscosity versus time at extension under conditions of constant strain velocities in molten polyisobutylene [23]

At high κ , stationary flow was not attained. The stationary flow was not detected, perhaps, because of limitations imposed by the experimental procedure. This can be exemplified by Ref. ¹⁷⁾ in which the stationary flow was not attained in the nonlinear region and which was detected only in Ref. ²¹⁾ at high degrees of extension.

In works where the stationary flow was detected, the viscosity $\tilde{\lambda} = \sigma/\kappa$ was, normally, either constant ^{16,20,31)} or grew with increase of κ ^{18,19,24-27)} above $3\eta_0$ (η_0 is the maximum shear viscosity) in the linear strain region. The intensive growth of viscosity $\tilde{\lambda}$ was detected, apparently, for the first time in Ref. ¹⁹⁾. The greatest increase in viscosity $\tilde{\lambda}$ from 3η to 20η was observed in Refs. ^{18,21,30)}. In the same works the viscosity $\tilde{\lambda}$ started to drop after the growth (this shall be discussed in detail below). Usually the relationship $\tilde{\kappa}/\dot{\eta}$ ($\dot{\eta} = \sigma_{12}/\dot{\gamma}$ is effective viscosity at stationary shear) is taken at different strain velocities, which could vary by more than an order of magnitude (see, for example, Ref. ³⁰⁾). The data on the existence of stationary flow and behavior of viscosity in this case, as well as descriptions of extended polymers are collected in Ref. ²⁰⁾.

Elastic strain in extension under conditions of $\kappa = \text{const}$ in most works (see ^{18-20,24,26)}) is a strictly increasing function of time with smoothly decreasing derivative $d(\ln \alpha)/dt$. In these cases the velocity of irreversible flow $e_p(t)$ strictly increases (exclusion detected in Refs. ^{23,24)} is discussed below). At stationary flow the elastic strain is constant and the irreversible strain velocity is $e_p = \kappa$. The higher κ , the more the share of elastic component is at fixed general strain ϵ .

A specific feature of curves given in Fig. 3 is the fact that the time during which the stationary flow is attained strictly decreases with increase of κ , while this is different in Refs. ^{18,24,34)} (see below).

2.2.3 Extension at Constant Force

Extension at force $F = \text{const}$ corresponds to conditions with intensively increasing stress. The stationary flow, in this case, is obviously not attained, and deformation,

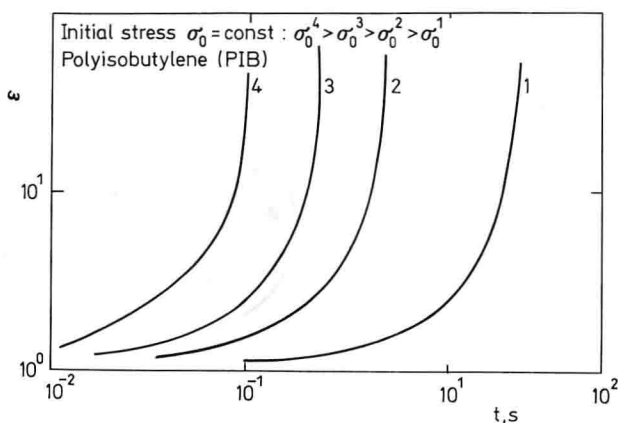


Fig. 4. Total strain ϵ versus time t in extension of polyisobutylene with different constant forces [23, 25]

sooner or later, leaves the linear region. The time of media staying in the linear region was estimated in Ref. ¹⁴⁾.

In extension under conditions $F = \text{const}$, dependencies of total strain ε and elastic strain α upon time t are measured as usual. In Refs. ^{11-13, 15, 35-38)} these experiments were arranged with polyisobutylene samples with different molecular weights and with low-density polyethylene (see below).

Dependencies of total strain $\varepsilon = l/l_0$ upon time t , in extension of polyisobutylene II-20 (USSR) at constant force F for different initial stresses $\sigma_0 = F/S_0$ (here S_0 is the cross-sectional area of the sample at $t = 0$) are given in Fig. 4.

In the region of t under investigation these dependencies are strictly increasing and practically independent of σ at low values of t . The higher σ_0 , the faster they grow with time.

2.2.4 Dependencies of Stress and Strain Velocities upon Elastic Strain

Let us consider also the regularities common for different types of extension. Dependencies of extension σ upon elastic strain α are given in Fig. 5. Continuous lines in Fig. 5 indicate dependencies $\sigma(\alpha)$ in extension at different constant strain velocities $\dot{\alpha}$. The higher $\dot{\alpha}$, the higher passes the dependency $\sigma(\alpha)$. The points with maximum α

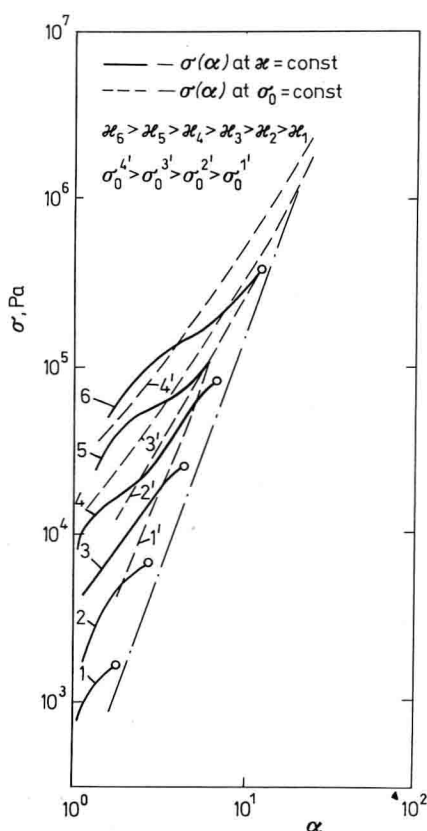


Fig. 5. Stress σ versus elastic strain α under different conditions of extension [23]