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# Handbook of Polymer Science and Technology

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Volume 3  
Applications and  
Processing Operations

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Edited by: Nicholas P. Cheremisinoff

# **Handbook of Polymer Science and Technology**

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Volume 3:  
APPLICATIONS AND PROCESSING OPERATIONS

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**Nicholas P. Cheremisinoff**

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Volume 3:  
APPLICATIONS AND PROCESSING OPERATIONS

# **Handbook of Polymer Science and Technology**

*edited by*

*Nicholas P. Cheremisinoff*

Volume 1 Synthesis and Properties

Volume 2 Performance Properties of Plastics and Elastomers

Volume 3 Applications and Processing Operations

Volume 4 Composites and Specialty Applications

*Other Volumes in Preparation*

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## Preface

Volume 3 describes end-use processing operations employed in the handling and manufacturing of rubber and plastic articles used in consumer-oriented applications. The book is comprised of fourteen chapters. The first two chapters are a continuation of Volume 2, aimed at describing the molecular and performance characteristics of ethylene-based copolymers. Chapter 2 extends discussions to terpolymer properties and provides an overview of consumer applications and processing operations employed in the fabrication of various rubber articles. This chapter serves to orient the user to more detailed discussions on specific processing operations. Chapter 3 provides a review of the property of thermoplasticity and its relation to processing. Chapters 4 and 5 relate to the flow dynamics of non-Newtonian materials, with the latter chapter describing the relationships between polymer molecular properties and flow deformation.

Detailed discussions on major unit operations of polymer processing are presented in the balance of this volume. Chapters 6 and 7 discuss the operations of calendaring and molding. Chapters 8 through 10 are devoted to mixing and extrusion. Chapters 11 and 12 provide further discussions on extruder-related topics, with criteria for die design and treatment of extruded polyethylene properties. Ultraviolet radiation for vulcanization is discussed in Chapter 13, and the final chapter provides detailed treatment of wire coating applications. Chapters discussing various unit operations are written to provide both a theoretical and practical design/scale-up approach to each processing operation.

The efforts of over twenty experts are presented in this volume. Their devotion to this work is greatly appreciated. In addition, the volume represents the advice and opinions of scores of engineers who provided suggestions on organization and content. Gratitude is also extended to Marcel Dekker, Inc., for the production of this volume.

*Nicholas P. Cheremisinoff*

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# Contents

<i>Preface</i>	<i>iii</i>
<i>Contributors</i>	<i>vii</i>
1. Structure of Ethylene Copolymers <i>I. G. Voigt-Martin and L. Mandelkern</i>	1
2. Properties and Uses of Ethylene–Propylene Rubbers <i>Nicholas P. Cheremisinoff</i>	113
3. Thermoelastic Effect in Polymers <i>Ernesto L. Rodriguez</i>	151
4. Thin-Film Flow of Pseudoplastic Liquids <i>Vujadin O. Popadić and Miodrag N. Tekić</i>	185
5. Effect of Polymer Structure on Polymer Flow <i>S. Ramachandran, H. W. Gao, and E. B. Christiansen</i>	199
6. Calendering Operations <i>Christian Kohlert, Dietmar Bothmer, and Wolfgang Kohlert</i>	271
7. Rubber Molding Methods <i>J. G. Sommer</i>	311
8. Applications of Continuous Mixers <i>Dilhan M. Kalyon</i>	373
9. Evaluating Screw Performance in Extrusion <i>Krzysztof Wilczynski</i>	421
10. Computer Modeling and Analysis of Extrusion Operations <i>Donald H. Sebastian</i>	443

11. Designing of Rubber Extrusion Dies	473
<i>Rengan Kannabiran</i>	
12. Properties of Solid-State Extruded Polyethylene	503
<i>Marcelo D. Failla and Jose M. Carella</i>	
13. Effect of UV Radiation on Polymers	541
<i>Christian Decker</i>	
14. Process and Simulation of Wire Coating	609
<i>Carlos Tiu, Anthony K. Podolsak, and Evan Mitsoulis</i>	
<i>Index</i>	649

# Structure of Ethylene Copolymers

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INTRODUCTION	1
EXPERIMENTAL TECHNIQUES	2
Light Scattering: Supramolecular Structure	2
X-Ray Scattering: Organization of Scattering Units	5
Electron Microscopy	11
Neutron Scattering	16
Raman Spectroscopy	19
STRUCTURE OF HOMOPOLYMERS	23
Supramolecular Structure	23
Structure of Solution-Grown Single Crystals	26
Structure of Crystals in Bulk	35
Structure of Interfacial Region (Interphase)	50
Structure of Liquid-like Region	51
STRUCTURE OF ETHYLENE COPOLYMERS	52
Supramolecular Structure	52
Structure of Solution-Grown Crystals	54
Structure of Crystals in Bulk	62
Structure of Interfacial Region	85
Structure of Liquid-like Region	86
THERMODYNAMICS OF CRYSTALLIZATION	87
Branching	96
Degree of Crystallinity	96
Other Random Ethylene Copolymers	99
Alternating Copolymers	104
SUMMARY	106
REFERENCES	106

## INTRODUCTION

The subject under discussion in this chapter concerns the structure of copolymers with particular emphasis on those based on ethylene. Therefore, we address those experimental

techniques that give this information directly. These include (1) light scattering, (2) x-ray scattering, (3) electron microscopy, (4) neutron scattering, and (5) vibrational spectroscopy. However, the interpretation of the data obtained by all these techniques involves certain assumptions and models that are not usually unique. In studying the published literature and evaluating the conclusions therein, it is important to know exactly where these assumptions are made and to decide whether they are justified. For this reason particular care has been taken to present a section surveying the experimental techniques.

Furthermore, the structure of copolymers is not a subject that can be surveyed completely out of context. The addition of comonomeric units into a chain has an effect on the structure that can be understood only within the framework of the structure of homopolymers. Added to this, the structure of solution grown crystals is highly relevant to the bulk material, where such crystals are embedded in an amorphous matrix. The problem regarding the exact manner in which these crystals are connected to one another and to the amorphous matrix is extraordinarily important for all physical properties of the bulk material. For this reason the structure of solution crystals has been discussed in some detail.

Finally, the experimentally determined structure has to be embedded into the general framework of our understanding of the thermodynamics of crystallization. For this reason a detailed section on thermodynamic analysis of polymer and copolymer crystallization is included.

From the point of view of crystallization behavior the definition of a copolymer can be rather subtle. The structure of a given chain molecule needs to be analyzed carefully to see if it satisfies the definition. Many different types of structural irregularities can be incorporated into the chain and can render it a copolymer from the present point of view. In a straightforward way, two (or more) chemically dissimilar monomers or co-units incorporated into the chain will constitute a copolymer. Depending on the nature of the repeating unit, there can be geometric or stereoisomers in the chain. In either case such a molecule properly constitutes a copolymer. There can also be head-to-head as opposed to head-to-tail structures in the chain. Branch points and crosslinks are other sources of structural irregularities.<sup>†</sup> Thus it is easily possible to have copolymeric behavior, from a crystallization point of view, with chemically identical units in the chain. Therefore, a careful study must be made of the chain structure of a given polymer before analyzing its crystallization behavior and properties. In addition to determining the type and amount of the structural irregularities that exist along the chain, we shall see that for very important reasons, their sequence distribution needs to be specified. The importance of the sequence distribution in determining the structure and properties of copolymers cannot be overemphasized.

## EXPERIMENTAL TECHNIQUES

### Light Scattering: Supermolecular Structure

A detailed description of the light-scattering technique has been given by Stein [4]. The samples are mounted between microscope slides and held in a universal stage to enable manipulation. The scattering pattern can be recorded using a photographic film or a

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<sup>†</sup> Although properly treated as structural irregularities, the influence of intermolecular crosslinks on the crystallization properties needs to be treated separately [1]. The reason for this is that resultant properties depend on the state that exists when the crosslinks are introduced [2, 3]. The analysis of this interesting but very specific situation is not given here because of space restraints.

suitable detector. Polarizer and analyzer are set up so that an  $H_v$  (incident light polarized vertically and scattered light polarized horizontally) or  $V_v$  (incident and scattered light polarized vertically) scattering pattern is recorded. Although the experimental setup is relatively simple, the interpretation of light-scattering patterns is by no means a trivial matter. Detailed theoretical calculations for scattering by spheres [5], disks [6], and rods [7] have been published elsewhere. The theoretical basis for scattering by spherulites has been presented by Stein [8]. The  $H_v$  scattering can be described by

$$I_{H_v} = C_3 V^2 \left\{ \frac{3}{U^3} (\alpha_t - \alpha_r) \cos^2 \frac{\theta}{2} \sin \mu \cos \mu [4 \sin U - U \cos U - 3(si)] \right\}^2 \quad (1)$$

where

$V$  = volume of the spherulite

$U$  = reduced angle  $[(4\pi R/\lambda) \sin(\theta/2)]$

$R$  = radius of the spherulite

$\mu$  = azimuthal scattering angle

$\alpha_r, \alpha_t$  = parallel and perpendicular components of the polarizability

and where

$$(si)U = \int_0^U \frac{\sin x}{x} dx \quad (2)$$

It is apparent from the equation for  $H_v$  that at a particular  $\mu$  (say,  $\mu = 45^\circ$ ) the intensity of scattering will go through a maximum with increasing scattering angle  $\theta$ . The intensity is zero at zero angle ( $U = 0$ ) and at large angles ( $U \rightarrow \infty$ ). A maximum occurs at  $U = 4.1$  corresponding to a scattering angle  $\theta_m$  given by  $4\pi(R/\lambda) \sin(\theta_m/2) = 4.1$ .

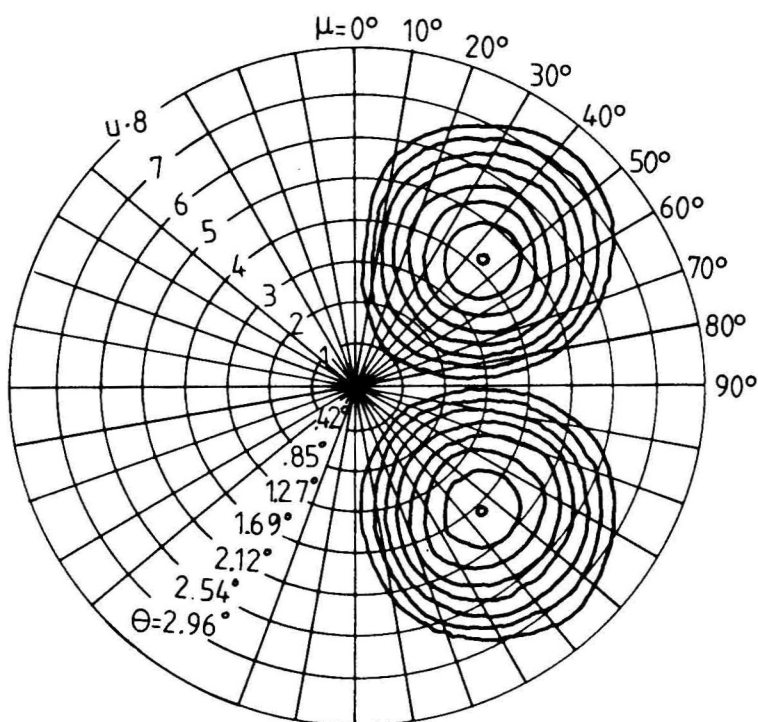
The determination of the scattering maximum thus affords a rapid means of determining the spherulite size. The pattern is clearly fourfold symmetric because of the  $\sin \mu \cos \mu$  dependence. Maxima occur at  $\mu = n/4 + n\pi/2$ . Such a pattern has the characteristic four-leaf-clover appearance (Fig. 1) and will be designated as type (a) spherulite. A variant of this pattern is observed where there is scattering present for  $\mu = 45^\circ$  at low angles. This type of scattering pattern has been described as "tennis racket" shaped and can be assigned to imperfections within spherulites, designated as type (b) [9]. Finally, further degeneration of the spherulite [type (c)] leads to a fourfold symmetry but no well-defined maximum for  $\theta$  at  $\mu = 45^\circ$ . SALS patterns are, however, frequently observed in polymeric films that do not exhibit any of the typical spherulitic features in the  $H_v$  scattering pattern, and various models have been calculated to account for the scattering features observed. The first of these models assumes a random assembly of anisotropic rods whose optical axis is inclined at an angle  $\omega_0$  with respect to the rod direction fixed in a plane defined by an azimuthal angle  $\delta$ . This scattering has been referred to in the literature as rod scattering [10]. It describes an anisotropic body such as a fibrillar arrangement of lamellar structures. For fixed  $\delta$  we can write [11]

$$I_{H_v} = K_1 \{ [\alpha(\theta) \sin^2 \mu \cos^2 \mu + \beta(\theta)] P_4(\cos \omega_0) A(U) + \delta(\theta) P_2(\cos \omega_0) B(U) + C(U) \} \quad (3)$$

where

$K_1$  = constant

$\alpha(\theta) = 420 \cos^2(\theta/2)$



**Figure 1** One-half the calculated scattered intensity contour for  $H_V$  scattering. (From Ref. 5.)

$$\beta(\theta) = 12 - 60 \cos^2(\theta/2)$$

$$\gamma(\theta) = 60 \cos^2(\theta/2) - 40$$

$$A(U) = (1/U^5)\{(U^3/6) - [(2U^2 - 1)/8] \sin 2U - (U/4) \cos 2U\}$$

$$B(U) = (1/2U^2)[1 - (\sin 2U/2U)]$$

$$C(U) = 28\{(\sin 2U/U)[(1 - \cos 2U)/2U^2]\}$$

$$U = (2\pi L/\lambda) \sin(\theta/2)$$

$P_4(\cos \omega_0)$  is a fourth-order Legendre function in  $\omega_0$ . For  $P_4 > 0$  or  $\omega_0 < 30^\circ 30'$  and  $\omega_0 > 70^\circ 07'$ , this pattern describes the figure  $\times$  and has been classified type (d) [10]. For  $P_4 = 0$ , the pattern is circularly symmetric and designated type (f). For  $P_4 < 0$ , the pattern describes the figure  $+$  and is designated type (e). In a generalization of this model,  $\theta$  is allowed to vary randomly, so that the model then corresponds to a situation in which the rods or fibrils are twisted about their fibrillar axes and the pattern is again type (d).

Both of these models contain the primary assumption that the rods have an infinitesimal width. Calculations have also been made which allow the rods in both models to have a finite width. In this case the fourfold symmetry becomes less well defined as the width of the rod is increased. The pattern becomes circularly symmetric as the width becomes comparable to the length. It is designated (g) since it represents a quite different scattering structure, although the pattern is similar to (f).

In the case of randomly arranged lamellae the scattering is circularly symmetric and is

designated (h). It can appear similar to rod patterns (g) and (h). The three situations must then be distinguished by polarized-light microscopy. It will be shown that numerous electron microscopy investigations have substantiated the general classification of morphologies in polyethylene fractions given originally by Maxfield and Mandelkern [12] while differing in detail. For example, “rod” scattering (d) does not arise from fibrils but from infinitely extended “roof”-shaped lamellae [13]. In samples giving rise to type (g) scattering, the lamellae are shorter. Type (h) scattering arises from large, randomly situated lamellae as well as from small, random crystallites. Finally, the spherulitic morphology shows more complex differences in inner lamellae arrangement than the three designations (a), (b), and (c) would indicate.

The situation regarding SALS can thus be summarized as follows: The scattering functions are extremely complex and can be interpreted only by means of models *that may not be unique*. Details of lamellar structure cannot be recognized, but a broad classification giving mutual lamellar arrangement is well supported by polarized light and electron microscopy.

### X-Ray Scattering: Organization of Scattering Units

X-ray scattering has been a very important tool in the structure investigation of polymeric materials. Since most polymers consist of crystalline and noncrystalline units—the latter being composed of interfacial and liquid-like structures—two regions of the scattering curve are of interest, namely:

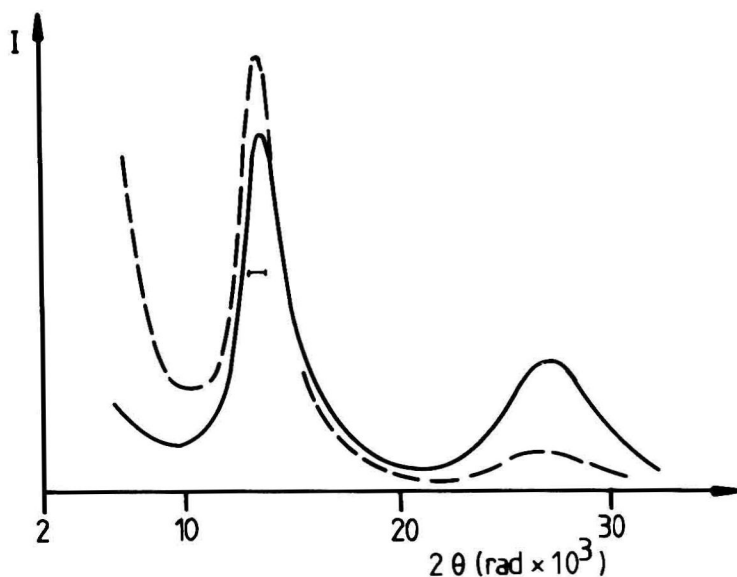
1. *Wide-angle range*: involves scattering angles  $2\theta$  which are greater than  $8^\circ$ . The information gathered from this scattering region concerns the dimensions of the unit cell, with distances in real space that are below  $10 \text{ \AA}$ .
2. *Small-angle range*: involves scattering angles below  $8^\circ$ . The information gleaned from this region concerns the mutual arrangement of crystalline and amorphous regions. If these are arranged such that the repeating units  $L$  (amorphous plus crystal thickness) are arranged in regular packets, an intensity maximum is obtained at an angle  $2\theta$  given by the Bragg relationship.

There are numerous standard textbooks on crystal structure determination (e.g., Refs. 14–16), so there is no need to discuss these here. The techniques of crystal structure determination are so well established that there have not been any serious discrepancies in establishing the unit cell and the space group of most crystalline polymers. Molecular crystals are often orthorhombic or monoclinic, but trigonal symmetry also occurs. The polymer chain is generally chosen to lie along the  $c$  axis. It may adopt a planar zigzag or a helical conformation. Details and literature references are given in a book by Wunderlich [17], in reference tables [18], and in an exhaustive survey by Miller [19].

The situation is not quite as clear with regard to small-angle x-ray scattering and there are some fundamental reasons for this, as shown in the following. Semicrystalline polymers generally give rise to small-angle x-ray diffraction patterns which are characterized by one or more diffuse maxima [20]. These are frequently converted into long spacings by simple application of Bragg's law. This procedure can lead to erroneous results.

The first source of error lies in the smearing effects inherent in slit-collimated small-angle x-ray cameras [21]. Details giving various procedures employed for slit-height correction are described in the literature [22–25]. Failing this, a point-collimated x-ray beam can be used, whereby the size of the beam should be restricted to minimize





**Figure 2** SAXS of PE single-crystal mat. Dashed line, observed; solid line, Lorentz corrected. (From Ref. 26.)

broadening of the scattering peaks. In fact, an ideal pinhole collimating system is difficult to achieve.

Even more difficult is the task of extracting information concerning lamella thickness distributions, nature and thickness of amorphous and transition regions, effect of lamellae curvature, and so on. On the assumption of an infinitely extended lamellar system, a Lorentz correction involving multiplication by  $s^2$  ( $s = 2 \sin \theta/\lambda$ ) is generally applied. Although the effect of this correction is not very large in highly regular systems such as single-crystal mats (Fig. 2), it is considerable for bulk material (Fig. 3). In cases where a second maximum is observed, it is frequently found that the ratio of the angles of the second and first maxima  $\theta_2/\theta_1$  is not 2. There are a variety of possible explanations for this [26].

In principle, there are two methods of approach to evaluate intensity distributions:

1. The true corrected intensity distribution is calculated from the measured distribution and compared with the intensity distribution obtained by Fourier transformation of a model structure.
2. The correlation function is calculated directly by Fourier transformation of the corrected measured intensity distribution. A discussion of the properties of correlation functions is given elsewhere [27].

Both methods involve uncertainties. Method 1 depends on the validity of the structural model adopted. Furthermore, the model is never unique. By an appropriate choice of various structural parameters, it is easily possible to obtain identical scattering curves. If a comparison with electron microscopy is made, the number of possible models is, of course, reduced. The advantage of this method is that the integration limits involved in