

ANALYTICAL CHEMISTRY OF POLYMERS

Part III. Identification Procedures and Chemical Analysis

Edited by GORDON M. KLINE

*National Bureau of Standards
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HIGH POLYMERS

A SERIES OF MONOGRAPHS ON THE CHEMISTRY, PHYSICS,
AND TECHNOLOGY OF HIGH POLYMERIC SUBSTANCES

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Part III

PREFACE

The Constitution of the United States gives the Congress authority to fix the standards for weights and measures; this responsibility has, in turn, been assigned to the National Bureau of Standards. This assignment is today much more complex and extensive than it was in the days when the only important measurements dealt with weight, length, and volume. Measurement standards must now be available in all areas of science and technology where physical and chemical measurements are important. It is therefore axiomatic that the National Bureau of Standards in fulfilling its statutory responsibility should be intensely concerned with all the important processes of measurement and must excel in precision measurement techniques.

In addition, scientific and industrial laboratories should be able to look to and properly expect from a national standards laboratory accurate determinations of the properties of basic materials. Thus, the provision of such data is also one of the NBS statutory functions.

In fulfilment of these responsibilities in the field of high polymers, Parts II and III of this book have been planned and written by staff members of the NBS Organic and Fibrous Materials Division to summarize our present knowledge of measurement techniques for the determination of structure and composition of macromolecules. Modern instrumental methods of analysis are stressed; many of these techniques have been undergoing active development and perfection during the period in which these chapters have been written, necessitating continuous revision and expansion of the coverage by the authors and editor.

Each chapter in Part II presents the basic theory underlying the application of an instrumental method of analysis to the exploration of the structure of polymers. This is followed by descriptive information on available equipment and procedural details. Comprehensive data are presented on the characteristics of polymers as determined by the various analytical techniques. Finally, the authors review the application of this information to analytical problems and to investigations of polymerization processes, polymer structure, stability, and related research.

Identification of polymers by systematic procedures, color tests, and microscopic examination are covered comprehensively in the first three

chapters of Part III. The two concluding chapters describe important developments in the application of radiochemical and end-group analysis to the unravelling of the complex composition of macromolecules. The subject matter of all chapters is fully tied to the published literature by extensive lists of references. These two volumes provide a broad review of developments in modern methods of polymer analysis, supplementing the information presented in Part I on the control methods used in the analytical laboratories of materials manufacturers.

The Director of the National Bureau of Standards, Dr. Allen V. Astin, stated recently: "The frontiers of measurement are the frontiers of science and technology; they are the frontiers of our knowledge of the physical world and our ability to make constructive use of that knowledge." The authors and editor have endeavored to explore in this book these frontiers for polymer science, a domain that in recent years has been the special subject of one or more new journals in each of the major countries of the world.

Again for Parts II and III, the editor wishes to record his deep appreciation and sincere thanks to his colleagues for their enthusiastic and meticulous contributions in their respective fields, to the editorial staff of the publisher for their efficient and effective handling of difficult copy, and to his wife, Dorothy, for her encouragement and patience during the several years of preparation of this book.

Washington, D. C.
June, 1961

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I. SYSTEMATIC PROCEDURES

G. M. BRAUER AND E. HOROWITZ, *National Bureau of Standards*

I. INTRODUCTION

A systematic scheme of testing is extremely valuable for completing a qualitative analysis of an unknown polymer with a minimum expenditure of time and effort. Many obstacles are encountered in developing such identification procedures for polymers. Usually, these materials have no sharp melting point and are soluble in a limited number of reagents. Commercial plastics may contain plasticizers, solvents, stabilizers, pigments, fillers, dyes, etc., which often must be removed before identification can be made. Presence of low molecular weight substances and catalyst fragments in the macromolecule, variations in the degree of branching and crystallinity, differences in monomer ratios in copolymers, stereospecificity, and grafting will change the physical properties and chemical behavior, and thus increase the difficulties of identification.

The most comprehensive systematic identification procedure for polymers was published in 1944 by Shaw (134). This procedure is based on the following steps: (1) purification of the polymer by removal of fillers, vehicles, or solvents, usually by methods based on differences in solubility; (2) division of the resin into groups by determination of the elementary composition, saponification number, and acetyl number; (3) distinguishing polymers in a given group by characteristics such as physical properties (density, refractive index, etc.), burning characteristics, solubility, and chemical classification tests.

Shorter schemes employing solely such tests as solubility, ignition behavior, or infrared spectra must be used with caution. The analyst will do well, however, to become acquainted with the many new analytical tools and procedures that have been developed in recent years and are described in various chapters of this book. Thorough knowledge of organic reactions and the structure and properties of polymers will allow many successful shortcuts of established procedures.

In the following pages, a few of the more comprehensive schemes of analysis are outlined. General identification schemes for organic com-

pounds such as those described by Cheronis and Entrikin (30), Huntress and Mulliken (74,75), McElvain (95), Openshaw (107), Schneider (128), Shriner and Fuson (137), and Smith and Shriner (147) should also be consulted. Many of these procedures can be readily applied to polymer analysis.

Various techniques employed for the characterization of polymers to obtain information as to the size of the polymer molecule, molecular distribution, degree of branching, copolymer segment length, etc., have been described by Allen (4).

Comprehensive treatments of the analysis of resin-based coating materials (78) and surface active agents (125) have recently been published. A number of other authors (119,148,174) have also reported procedures for the identification of surface active agents which may be present in polymers.

II. PREPARATION AND SEPARATION OF SAMPLE

1. Preparation of the Sample

A representative sample must be selected for the analysis. It is usually desirable to reduce the material to a powder. Sometimes the material can be crushed in a mortar. If that is not possible, filing, turning on a lathe, or cutting in a mill may be useful. Great care should be taken that the material does not become hot during the pulverization; otherwise, changes in the chemical composition may occur.

2. Separation of Constituents

The success of the analysis will often depend on the ability of the chemist to isolate in nearly pure form the various constituents of a mixture. Accordingly, it is desirable and often imperative to isolate the individual polymers in as pure a form as possible before attempting ultimate analysis.

Some polymeric materials have a rather complex composition. Commercial vinyl chloride plastics, for example, contain the basic polymer or copolymer, plasticizers, stabilizers, pigments, lubricants, fillers, and residues of surface active agents.

The principle used repeatedly in the analysis of plastic materials is the solution of the polymer in one solvent followed by precipitation by addition of a nonsolvent. The subsequent examination of the recovered polymer or of the additive remaining in solution can then be accomplished.

The most commonly encountered problem is the separation of filler and plasticizer from the base plastic. The plasticizer can be removed by

means of a suitable solvent such as ether or some other low-boiling liquid. Every effort should be made to select a solvent that will remove the plasticizer only. Liquids that react with the polymer, partially dissolve it, or are strongly absorbed must be avoided.

Resin and plasticizer may be separated from inorganic fillers by dissolving the mixture in a solvent, preferably using an extraction apparatus. The undissolved residue in the extraction thimble should be tested for the complete removal of the polymer. Successive fractionation employing other solvents or solvent mixtures to obtain complete separation may be necessary. The polymer in the extract may be recovered by precipitation by the slow addition of a nonsolvent that is a solvent for the plasticizer or by distilling off the extraction liquid. The proper solvents are selected by trial and error or on the basis of some prior knowledge of the material. If a quantitative determination of the purified polymer is required, the material can be dried, preferably in a high vacuum, and weighed.

Separation of the filler by extraction methods is not feasible for the thermosetting insoluble plastics. In this case, modification of the polymer such as by hydrolysis or esterification may be helpful. Sometimes removal of an organic filler that has nearly identical properties with the plastic is not possible. Microscopic examination of the specimen will usually detect the presence of such a constituent.

The separated filler can be investigated microscopically. Inorganic constituents are determined by the customary chemical or spectroscopic analytical procedures.

Isolation of resins dissolved in volatile solvents may be accomplished by precipitation or by distillation at atmospheric or reduced pressure. If the solvents are immiscible with water, steam distillation can be used. The nonvolatile medium is extracted from the residue with ether or other suitable solvent.

Emulsions must first be broken before their ingredients can be separated. This can often be accomplished by coagulation with nonsolvents or inorganic salts, or by dialysis. In some cases coagulation can be accomplished by cooling to below the freezing point of water.

The separation of pigment and vehicles in paints (62) may be accomplished by the usual methods, such as centrifuging. When the vehicle alone is of interest, Bradley (25) describes a simple method of removing the pigment.

For example, enamel (1 qt.) is diluted with acetone and approximately 200 g. of kieselguhr to a volume of 1 gal. This mixture is well stirred and a portion is poured into a Büchner funnel previously fitted with a medium

grade of filter paper. Vacuum is gradually applied until an efficient filter bed has been prepared, and the first portion of the filtrate is returned for refiltration. The remainder is then filtered. If the filtrate is still cloudy, it is again mixed with kieselguhr and refiltered. The residue of pigment and kieselguhr may be mixed with a fresh portion of acetone and again filtered, the second filtrate being combined with the first. If necessary, the filtrate may finally be passed through a fine grade of filter paper to obtain complete and final clarification. If acetone is observed to cause precipitation or coagulation of the vehicle, a mixture of equal volumes of acetone and benzene or other low-boiling solvents may be substituted. The acetone or other low-boiling solvent used is removed by distillation on a water bath.

Polymer, free from fillers and plasticizers, may contain low molecular weight constituents such as remnants of catalysts, activators, modifiers, emulsifiers, stabilizers, etc. Many of these impurities can be removed by solvent extraction.

Mark (93) reported that a relatively good purification of synthetic polymers can be accomplished in the following manner:

Make a 1-2% solution of the polymer in a not too high boiling solvent, pass it several times through a glass filter, and precipitate the polymer at elevated temperature with an appropriate precipitant. In the case of polystyrene use, for instance, benzene or toluene as solvent and isopropanol as precipitant. Separate the precipitate from the supernatant liquid by decantation, filtration, or centrifugation, and wash the precipitate with hot precipitant. Dissolve the polymer in another solvent (methyl ethyl ketone in the case of polystyrene) and precipitate with a low-boiling precipitant (methanol in the case of polystyrene). Again wash the precipitate and repeat the whole procedure. Finally, dry the precipitate slowly under vacuum at room temperature.

When fractions of several polymers (cellulose acetate, cellulose nitrate, polystyrene, polyvinyl chloride, etc.) were deliberately contaminated with various low molecular weight substances, it was found that most of the impurities could be removed by the above procedure to the point where they could not be detected by standard analytical methods. The most critical step in the whole procedure is the final drying, because it may lead to irreversible changes of the polymer (crosslinking, degradation). It appears essential to use in the last precipitation a very volatile precipitant which can be easily removed under vacuum at low temperature.

A method for the separation of polymers from solvents and monomers by a freezing technique is described by Lewis and Mayo (87) as follows:

Dissolve the polymer in 8 to 10 times its weight of benzene in an Erlen-

meyer flask and freeze the solution quickly in dry ice. Transfer the flask to an ice bath held at 0°C. and 1 mm. pressure. Sublime the benzene slowly from the polymer without melting the benzene or sintering of the polymer; 8-10 hours are usually required for removal of most of the benzene. The polymer is left as a soft, fluffy, very porous solid. After the benzene has been largely removed at 0°C., let the product stand at room temperature in a high vacuum for a few hours before heating in order to avoid sintering caused by small residual amounts of solvent. Conduct the final drying at 70-100°C. in a high vacuum depending on the polymer to be purified; the higher the final temperature, the faster constant weight is attained.

The upper temperature that may be used is determined by the temperature at which the polymer sinters and loses its porous structure. For instance, polystyrene sinters slowly at 100°C., the porous cake shrinking to perhaps half its original volume in 10 hours. Since the whole procedure is carried out at reduced pressure, no difficulties arise from oxidation or moisture adsorption. Some chlorine-containing compounds lose hydrogen chloride under these conditions. Solvents other than benzene which are conveniently sublimed can also be employed.

3. Determination of Purity

One of the most difficult problems in polymer chemistry is the determination of the purity of the sample. Direct analysis by chemical or physical procedures for probable contaminants is most commonly conducted.

Determinations of volatile matter such as moisture or solvents or for noncombustible constituents (usually inorganic) in polymers can be readily conducted. Functional groups other than those that should be present can be detected or quantitatively estimated by various procedures, involving chemical or instrumental techniques some of which are described in Part II.

Traces of monomer in polymers can be detected by a variety of techniques such as end group analyses or physicochemical procedures. Quantitative determination of monomer content in the polymer can be conducted by the freeze-drying technique of Lewis and Mayo (87), described in Section II-2. The volatile products are trapped and the monomer content is determined by an appropriate method. Monomer content in acrylic and some allyl or vinyl polymers can be estimated by halogen addition to the carbon double bond, using aqueous bromide-bromate reagent which, on acidification, releases bromine (1).

A check of the purity and homogeneity can also be obtained if the prop-

erties of the polymer are unaffected by the application of such separation procedures as crystallization, precipitation, extraction, distillation, chromatography, or possibly zone refining. If no solvent or other material is added, a difference in observed properties before or after fractionation or between fractions shows the presence of impurities or nonhomogeneity of the sample.

Assay of the main constituents by analysis for elementary composition, measurement of physical or optical properties, or degradation behavior also gives an indication of the purity, provided the structure of the major component is accurately known and the precision of the particular measurement is high enough to detect possible impurities. For crystalline materials of narrow molecular weight spectrum, purity determinations based on freezing point, thermogravimetric or differential thermal analysis, or solubility curves may be useful. A discussion of the various techniques is given by Stenger, Crummett, and Cobler (153).

III. PHYSICAL TESTS

1. Preliminary Examination

The polymer sample, free from interfering matter, should be subjected to a rigid preliminary examination of physical properties. The physical appearance and qualitative aspects of some physical characteristics are useful guides for identification. The physical state, color, transparency, and odor should be noted. It should be determined whether the material is amorphous or crystalline. Such criteria as sharp melting point, sharp X-ray diffraction pattern, insolubility in at least some common solvents, high toughness rather than high degree of elasticity, and necking down on cold drawing indicate the polymer is at least partially crystalline. Surface imperfections or inhomogeneities can often be detected readily under a microscope. The polymer should be stretched, if possible. Materials such as polyvinyl acetate, polyacrylates, rubber, elastomers, and plasticized thermoplastics are quite extensible. Hardness can be judged by attempting to mar the sample with the thumbnail or a coin. A comparison with a known polymer is often helpful. Thus, polymethyl methacrylate is difficult to mar with a thumbnail. Transparent cellulose acetate mars readily. Polystyrene gives a peculiar metallic ring when dropped; no other plastic behaves in the same manner.

Fibers or yarns should be broken and the strength and extensibility noted. Good strength with little extensibility suggests highly oriented fibers or, perhaps, glass fibers. Glass fibers will be indicated by their rapid