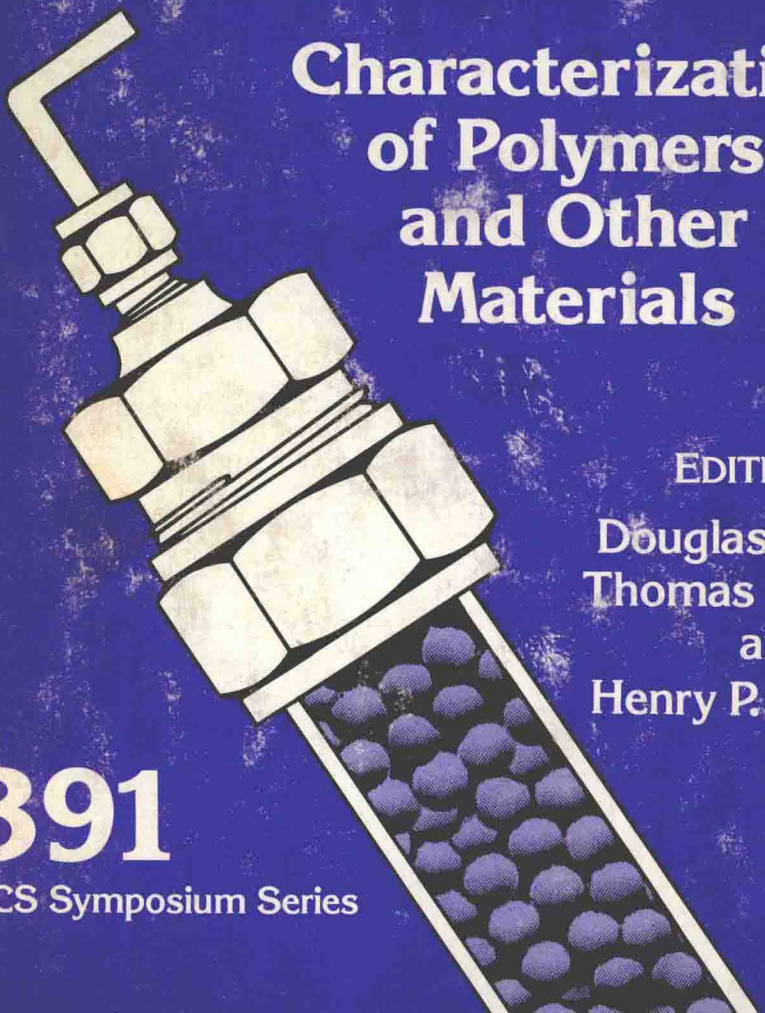
Inverse Gas Chromatography

Characterization of Polymers and Other Materials



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Inverse Gas Chromatography

Characterization of Polymers and Other Materials

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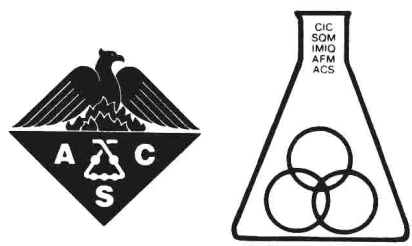

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Foreword

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation.

Preface

INVERSE GAS CHROMATOGRAPHY (IGC) is a useful technique for characterizing synthetic and biological polymers, copolymers, polymer blends, glass and carbon fibers, coal, and solid foods.

The technique involves creating within a column a stationary phase of the solid material of interest. The stationary phase may be a thin polymeric coating on an inert substrate, a finely divided solid, or a thin polymeric coating on the column wall. A volatile *probe* of known characteristics is passed through the column via an inert mobile phase and the output is monitored. The residence time of the probe and the shape of the chromatogram indicate the characteristics of the stationary phase and its interaction with the probe. Thus, IGC is a variation of conventional gas chromatography.

IGC can be used to determine various properties of the stationary phase, such as the transition temperatures, polymer–polymer interaction parameters, acid–base characteristics, solubility parameters, crystallinity, surface tension, and surface area. IGC can also be used to determine properties of the vapor–solid system, such as adsorption properties, heat of adsorption, interaction parameters, interfacial energy, and diffusion coefficients. The advantages of IGC are simplicity and speed of data collection, accuracy and precision of the data, relatively low capital investment, and dependability and low operating cost of the equipment.

Increased interest in IGC has resulted in a dramatic increase in the number of papers on the subject. In the decade following the first mention of IGC in 1967, approximately 30 papers were published about IGC. In the ensuing decade, more than 300 IGC papers were published. This book, the first to focus exclusively on IGC, contains 19 of the 20 papers presented at the Symposium on Polymer Characterization by IGC. Three chapters were added to broaden the scope of this volume.

Following an overview of this volume, the first section, which consists of three chapters, focuses on methodology and instrumentation. The next three sections consider characterization of vapor–polymer systems (4 chapters), polymer–polymer systems (4 chapters), and surfaces and interfaces (6 chapters). The final two sections cover analytical applications (2 chapters) and the application of IGC in coal characterization and food science (1 chapter each).

Each chapter of the volume was critiqued by at least two scientists (in addition to the editors) and revised accordingly by the authors. The editors appreciate the assistance provided by the reviewers and by Cheryl Shanks of the ACS Books Department. Finally, the editors gratefully acknowledge the magnificent job done by our associate editor, Clara C. Pizaña, in copy editing manuscripts and assisting in the final production stages of the book.

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Chapter 1

Overview of Inverse Gas Chromatography

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Inverse gas chromatography (IGC) is an extension of conventional gas chromatography (GC) in which a non-volatile material to be investigated is immobilized within a GC column. This *stationary phase* is then characterized by monitoring the passage of volatile *probe* molecules of known properties as they are carried through the column via an inert gas. The invention of IGC in 1967 (1) and the subsequent development of IGC theory and methodology, beginning in 1976 (2) and continuing today, are the consequence of the increasing interest in materials science. While IGC was initially used only in the study of synthetic polymers, today, as evidenced in this book, IGC is used to study synthetic and biological polymers, copolymers, polymer blends, glass and carbon fibers, coal, and solid foods.

Laub (3) estimates that in the decade prior to 1977, IGC related publications contributed only approximately 3% of the total of some 1400 devoted to the overall subject of gas chromatography. In an update, soon to be published (3), Laub notes that in the decade prior to 1987, the total number of GC papers has remained about the same, but IGC now accounts for some 300 of these, or nearly 30% of the total. These statistics alone suggest the desirability of symposia in which the most recent advances in theoretical and practical aspects of the IGC methodology are represented.

Reasons for IGC's higher profile in the technical literature include convenience and economics of operation. The basic tools for IGC are inexpensive, rugged, widely available, and as well suited for routine laboratory applications, as they are for demanding fundamental research. IGC data may be collected quite rapidly over extended temperature ranges. A variety of probes may be used in the mobile phase to elucidate the characteristics of the stationary phase, characteristics that otherwise are only obtained at far greater expenditure of time and money.

Perhaps a more important motivator for the increasing use of IGC is the method's flexibility and potential for generating data useful in the broad domain of polymer physical chemistry. Key to this consideration is the relationship between thermodynamics and the fundamental datum of IGC, the specific retention volume, V_g. The relationship has been

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discussed in detail elsewhere (4-8). In the present volume, Guillet and co-workers (9) demonstrate that the link between V_g and enthalpies of interaction and between the IGC datum and χ, the Flory-Huggins interaction parameter for polymer/probe pairs (10), is intrinsically valuable. Once again, IGC is a convenient route to information that is otherwise difficult to obtain and frequently unattainable. In all conventional experiments capable of measuring the interaction thermodynamics of polymers, such as swelling resulting from solvent uptake, neutron scattering, and changes in colligative properties, the polymer phase is highly diluted. In contrast, IGC measures interaction quantities at high polymer concentrations, thereby adding a considerable measure of practical relevance to IGC as a tool for materials science. Since a wide temperature range often is accessible, the important question of temperature dependence for χ can be resolved, at least in principle, without recourse to hypothesis or approximation.

The most vital element in the growth pattern of IGC is found in the breadth of applications. Aside from providing thermodynamic information, the IGC technique remains an excellent source for determining phase transitions, for measuring adsorption properties, and for estimating dispersive and non-dispersive forces acting at surfaces and interfaces. Given this spectrum of applications and the continued growth of materials science, it is reasonable to conclude that IGC methodology will continue to play an important role in furthering an understanding of materials behavior, and in helping to design multicomponent systems that meet desired targets of performance and durability.

Methodology and Instrumentation

IGC lends itself to automation and to computerized data processing, thereby enhancing the attractiveness of IGC as a laboratory technique. Guillet and co-workers report here on the automation of IGC temperature scanning, a measure certain to prove useful for routine determinations of retention data over broad temperature ranges (9). The application of algorithms to stimulate IGC behavior patterns by computational methods, as addressed here by Hattam, Du, and Munk (11), suggests that mathematical modeling of retention characteristics may develop along lines already well established in polymer processing. Consequently, for given combinations of stationary and volatile phases, adsorption, absorption, and diffusion patterns may be predicted and interpreted in terms of evolving concepts of component interaction.

A further significant trend in IGC technology is the variety of forms in which the stationary phase may be prepared. Elsewhere in this volume, Bolvari, Ward, Koning, and Sheehy (12) describe in detail two common methods for creating polymeric stationary phases. The most common methodology consists of depositing a thin polymeric coating on small, inert spheres and packing the column with the coated spheres. The second method, described in detail by Bolvari et al. (12), consists of depositing a thin polymeric coating on the inside wall of the column. Purportedly, the sensitivity and reliability of IGC can be improved by using the *capillary chromatography* approach. Matsuura and co-workers (13) use a simpler approach to creating a polymeric stationary phase; they use a finely divided and sieved polymer powder. This approach is similar to that used to study glass and carbon fiber stationary phases. Again, Bolvari et al. (12) describe in detail the methodology for creating a stationary phase of short fiber fragments as well as long, continuous fiber lengths.

Sorption and Diffusion in Polymers

Sorption and diffusion in polymers are of fundamental and practical concern. However, data acquisition by conventional methods is difficult and time consuming. Again, IGC represents an attractive alternative. Shiyao and co-workers, concerned with pervaporation processes, use IGC to study adsorption phenomena of single gases and binary mixtures of organic vapors on cellulosic and polyethersulfone membrane materials (13). Their work also notes certain limitations to IGC, which currently restrict its breadth of application. Notable is the upper limit to gas inlet pressure, currently in the vicinity of 100 kPa. Raising this limit would be beneficial to the pertinent use of IGC as an indicator of membrane-vapor interactions under conditions realistic for membrane separation processes.

Demertzis and Kontominas investigate the diffusion of water in polyvinylidene chloride polymers and copolymers, a subject of great importance in the area of packaging films (14). They note that most of the data on diffusion have been obtained by time consuming static methods requiring extensive data analysis. Although their work was limited to low concentrations of the diffusing molecules, the speed and convenience of obtaining diffusion coefficients and thermodynamic parameters relating to the sorption process are noteworthy features. Finally, Arnould and Laurence report on measurements of diffusion coefficients in polymethyl methacrylate of small species including methanol, acetone, alkyl acetates, and various aromatic hydrocarbons (15). The flexibility of IGC is demonstrated again by the breadth of the temperature range used in this work. The capillary IGC experiments lead to interpretations of the relationship between the size of the diffusing molecule and the diffusion coefficients, and provide a convenient data base for advancing diffusion theory for polymeric membranes.

Interaction characteristics in polymer-related areas frequently make use of solubility parameters (16). While the usefulness of solubility parameters is undeniable, there exists the limitation that they need to be estimated either by calculation or from indirect experimental measurements. The thermodynamic basis of IGC serves a most useful purpose in this respect by making possible a direct experimental determination of the solubility parameter and its dependence on temperature and composition variables. Price (17) uses IGC for the measurement of accurate χ values for macromolecule/vapor pairs, which are then used for the evaluation of solubility parameters for a series of non-volatile hydrocarbons, alkyl phthalates, and pyrrolidones. It may be argued that IGC is the only unequivocal, experimental route to polymer solubility parameters, and that its application in this regard may further enhance the practical value of that parameter. Guillet (9) also notes the value of IGC in this regard.

Polymer Blend Characterization

The suitability of IGC as a route to interaction thermodynamics using non-volatile stationary phases and selected probe molecules at high dilution has been noted above. Much valuable information on the miscibility of solvent-polymer systems, derived from IGC measurements, continues to be published in the literature. However, equally important is information on the state of interaction among the non-volatile components of complex polymer-containing systems. Such information is an invaluable guide to the formulation of polymer blends and fiber- and particulate-reinforced polymer compounds, and would appear to have at least equal relevance to the properties of high performance, non-

polymeric composite materials. Other important and rapidly-growing areas of science, such as bioengineering, also would be well served by a convenient experimental method for the thermodynamic characterization of relevant materials.

In theory, IGC is well suited for the study of mixed polymer systems (18-22) and must be considered along with traditional methods for measuring polymer-polymer interactions (23), such as melting point depression (24), heat of mixing (25-27), cloud point (28-30), light scattering (31), osmotic pressure (32), and interdiffusion via forward recoil spectrometry (33-35). By using IGC, polymer mixtures may be studied over the entire composition range and at all accessible temperatures. However, in practice it is found that the interaction parameter for a pair of stationary phase components, generally written χ_{23}, is not uniquely defined for a given polymer composition and temperature. Rather, it varies with the selection of probe, thereby creating a dilemma that is yet to be resolved fully. Conceptually, such variations should not be entirely surprising. IGC tests the interaction thermodynamics at polymer/polymer contacts by injecting a small amount of sensing or probe molecules. Unless the volatile phase molecule partitions randomly between the components of the stationary phase, some perturbation in the energies at polymer/polymer contacts should be expected. Indeed, it might be argued that the thermodynamic system is changed by each incidence of non-random partitioning. The measured value of χ_{23} would then be valid for each specific system as defined by the polymer mixture and the probe. However, it should not be regarded as an unequivocal measure of the thermodynamic state pertaining to the polymers alone.

The importance of applying IGC to the interaction thermodynamics of polymers is well illustrated by the content of the present volume. While a general solution to the probe dependence problem may not yet be available, what may be called interim approaches are followed by diPaola-Baranyi (36) and by Klotz and co-workers (37). Here, the probe-to-probe variations of χ_{23} in the system polystyrene/poly(2,6-dimethyl-1,4-phenylene oxide), (PS/PMMPO) are acknowledged. Both authors found the variations to be non-systematic, therefore justifying a simple averaging procedure. Significant differences are found in the interaction numbers reported by these authors, the averaging process notwithstanding. The miscibility question is also investigated for other polymer blends by diPaola-Baranyi, again relying on an averaging procedure for the calculation of interaction parameters.

Munk and co-workers have been concerned with the above-stated problem for some time (38, 39). In this volume (40), their attention is focused on miscible blends of polycaprolactone and polyepichlorohydrin. These authors demonstrate that to a considerable degree the probe variation problem can be mitigated by scrupulous attention to experimental details in the IGC methodology. This concern for details is required at any rate, if the high data reproducibility needed for meaningful studies of interaction in miscible polymer blends is to be attained. These details center on modified methods for coating polymers onto solid supports, on improved methods for measuring carrier gas flow rates, and on enhanced, computer-based data analyses of elution traces. Also, corrections are made for contributions to retention times from uncoated support material. More than twenty volatile probes are used by Munk, and the probe-to-probe variations in χ_{23}, while not entirely absent, are much less apparent than they would be under standard experimental protocols.

Since relatively slight variations in interaction parameter values can cause significant shifts in the degree of component miscibility, the demand for high accuracy in IGC measurements is paramount. Su and Fried (41) have applied the modifications first

suggested by Munk (38, 39) to their work on blends using polystyrene, poly(4-methylstyrene), and PMMPO. They found evidence for thermal degradation in PMMPO when columns of this polymer were exposed repeatedly to temperatures in the span 200 to 280°C. Therefore, they identify another potential source of difficulty to be heeded if the true potential of the IGC route to interaction thermodynamics in polymer mixtures is to be realized.

Clearly, the use of IGC to generate formal thermodynamic information brings into play, first, the method's great convenience and flexibility, and second, the limitations imposed by the cited volatile-phase dependencies. It is likely that a full resolution of the problem hinges on a more rigorous definition of the thermodynamic terms that pertain to binary polymer systems. According to Sanchez (42), when compositional dependencies are encountered, then a full description of polymer mixture thermodynamics requires the definition of four different χ parameters. One χ is associated with the free energy, two are related to the first concentration derivative of the free energy, and the fourth χ is related to the second concentration derivative. The procedure needed to obtain these parameters involves using appropriate equation-of-state models and theoretically derived Henry's law constants for the process of gases sorbing on polymer solids. Sanchez (42) derives such constants and suggests that when applied to IGC, their use will produce bare interaction parameters, independent of mobile phase composition. Developments along these, or related lines, will provide further impetus to the important task of clarifying the thermodynamic criteria of interaction in multicomponent polymer systems, and to the important part to be played in that task by IGC.

Surface and Interface Characterization

Because of the current emphasis on high performance reinforced polymer composites, much attention is being placed on fiber-reinforced polymer matrices as subjects of study. This attests to the great importance of the interface and interphase in determining the properties of such systems, and on the relatively sparse information currently available on the subject. The concept of acid/base interactions across the fiber-polymer interface is noted particularly. The relevance of acid/base theories to the behavior of polymers at surfaces and at interfaces has been studied by Fowkes (43), among others, using laborious calorimetric measurements of interaction enthalpies (43). Once again, data acquisition via IGC appears to be sufficiently rapid and accurate to have generated appreciable advances. A good illustration of IGC's pertinence to the matter is documented by Schultz and Lavielle, who use dispersion force probes along with volatiles known to act as Lewis acids or bases, to evaluate the dispersive and non-dispersive force contributions to the surface energies of variously surface-treated carbon fibers (44). They use the Gutmann theory (45) to obtain acceptor and donor numbers for their substrates, as well as for an epoxy matrix. The adhesion of the fiber-matrix interface depends clearly on the measured strength of acid/base interactions.

Carbon fiber reinforced composites are at the forefront of current developments in polymer composites, and there is additional evidence for the important role being played by IGC in characterizing the interface in such systems. The Gutmann theory is used by Bolvari and Ward, who report acid/base interactions for surface-treated carbon fibers and a series of thermoplastic polymer hosts, including polysulfone, polycarbonate, and

polyetherimide (46). Once again, strong acid/base coupling is found to be beneficial to the strength of the interface. Wesson and Alfred investigate carbon fibers (47) and compare the surface properties of graphitized carbon fibers with sized versions and with fibers treated in radio-frequency glow discharges (plasmas). In addition to demonstrating the effects of surface modification procedures on surface acid/base character, the IGC technique is used to produce adsorption isotherms for the fiber substrates. In this manner, site energy distributions are obtained that emphasize differences between the uniform surface energetics of the graphitized fiber and the sized or plasma-treated versions.

Since IGC is able to generate adsorption isotherms and to evaluate acid/base interactions for specified adsorbate-adsorbent pairs, it follows that the technique is able to develop a detailed picture of surface properties for non-volatile stationary phases. This is illustrated, again for carbon fibers, by Vukov and Gray (48). They combine IGC information at essentially zero coverage of the injected probes with finite concentration data to obtain heat of adsorption values ranging from zero to multi-layer coverage. Their meticulous study shows the effects of thermal pretreatment on fiber surface characteristics, and underscores the convenience and power of IGC to generate information otherwise far more difficult to obtain.

A further illustration of IGC as a source of data for acid/base characterization of polymers and of solid constituents of complex polymer systems, is given by Osmont and Schreiber (49), who rate the inherent acid/base interaction potentials of glass fiber surfaces and of polymers by a comparative index, based on the Drago acid/base concepts (50). The interaction index is conveniently measured by IGC and is shown to differentiate clearly among untreated and variously silane-modified glass fiber surfaces. Conventional methods are used to determine adsorption isotherms for fiber-polymer pairs, and the IGC data are used to demonstrate the relationship between acid/base interactions and the quantity of polymer retained at fiber surfaces.

The applicability of IGC to particulates, used as pigmenting or reinforcing solids in polymer matrices, has been noted above. In surface coatings, pigment-polymer interaction may strongly affect adhesion, mechanical integrity, and durability of protective polymer films. The use of IGC on particulate substrates is illustrated in this volume by Papirer and co-workers (51). They characterize the surface properties of high surface area silicas both as supplied by manufacturers and as surface modified by grafting to them alkyl, diol, and polyethylene glycol moieties. The grafting procedures are shown to lead to important changes in donor-acceptor properties and consequently to the suitability of these particulates as reinforcing materials for polymer or elastomer matrices. Papirer's work also demonstrates the feasibility of relating surface characteristics obtained by IGC with independent surface analyses produced by nuclear magnetic resonance and X-ray photoelectron spectroscopy. The correlations attest to the validity of IGC techniques as surface diagnostic tools.

Guillet (9) uses IGC to estimate the degree of crystallinity in semicrystalline polymers and to compute the surface area of polymer powders. Linear polyethylene is used as the vehicle to demonstrate the former application. In the latter, a requisite is to evaluate the partition coefficient for a selected probe/polymer combination (n-decane/PMMA in the present instance). Once this is obtained via IGC, simple retention time measurements become suitable as routine analytical or control methods to monitor surface areas in polymer powders.

Analytical Applications

Laub and Tyagi investigate the analytical qualities of GC in general, and IGC specifically (52). They demonstrate the value of family retention plots from which the elution behavior of homologues or of related compounds in a series of volatile phase components may be estimated. In this way, the separability of such compounds via IGC methods is readily predicted. Also noted is the economy of sample sizes required for IGC, an invaluable consideration when only minute quantities of material are available.

One variant of IGC is pulsed chromatography, which allows for a monitoring of changes brought about in a stationary phase by chemical, environmental responses, and the like. Raymer and co-workers use deuterated tracers in pulsed chromatography to study the sorption of polar and non-polar probes on various imide-based polymers (53). A specific aspect of the study centered on the influence of water on the retention characteristics of given polymer/probe pairs. Emphasis is placed on the potential value of the technique in determining break-through volumes of specific molecules for selected polymer barrier structures.

Special Applications

Neill and Winans (54) and Gilbert (55) demonstrate the applicability of IGC to systems other than synthetic polymers and fibers. These workers have expanded the use of IGC to include research involving naturally-occurring materials. Using a column packed with a mixture of finely divided coal and non-porous glass beads, Neill and Winans (54) utilize IGC to follow the chemical and physical changes that occur when coal is heated in inert atmospheres. They are able to observe differences in transition temperatures and enthalpies of sorption for the different coals studied. Gilbert (55) applies a modified frontal analysis method to study water sorption kinetics in biological macromolecules. By doing so, Gilbert avoids having to apply equilibrium assumptions to these systems, which are influenced by entropic as well as enthalpic considerations.

Conclusion

This overview outlines some of the important basic concepts implicated in IGC, notes some of the strengths and limitations inherent in the technique, and mentions at least the more active areas of application for IGC. In a field as fertile and as rapidly changing as IGC, comprehensiveness would entail lengthy discussion, and ultimately would fail to account for all that is noteworthy. An attempt has been made to stress the breadth of possible applications for IGC, and this supports the tenet that the method will continue to play an expanding role in the science and technology of polymers and of advanced materials in general. It is regrettable that a book of the present size and scope can sample only a small fraction of the total output in IGC. One may look forward with confidence to the further evolution of a methodology at once subtle yet simple and convenient, at once rigorous in its thermodynamic basis and useful for analytic or quality-control objectives. The growth rate in IGC, alluded to at the beginning of this overview, will no doubt be maintained in the future. If that projection is correct, then future volumes of this kind will no doubt follow.