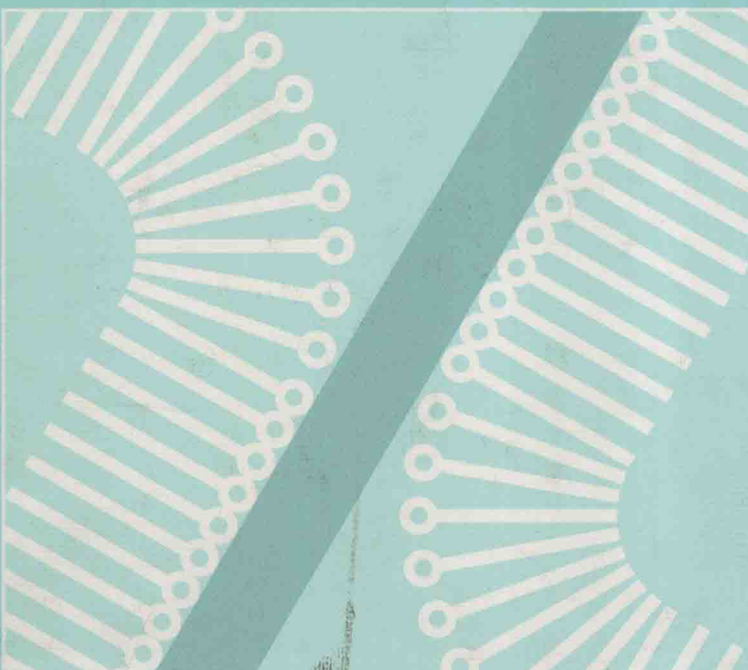
Polyimide Membranes

Applications, Fabrications, and Properties

H. Ohya, V. V. Kudryavtsev, S. I. Semenova



Kodansha

Gordon and Breach

Polyimide Membranes

—Applications, Fabrications, and Properties

by

Haruhiko Ohya
Dept. of Material Science & Chemical Engineering, Yokohama National University, Yokohama 240, Japan

Vladislav V. Kudryavtsev
Institute of Macromolecular Compounds, Russian Academy of Science, Russia

and

Svetlana I. Semenova
Polimersintez, Vladimir, Russia

Kodansha

Tokyo 1996

Gordon and Breach Publishers

Australia · Canada · China · France · Germany · India · Japan · Luxembourg · Malaysia · The Netherlands · Russia · Singapore · Switzerland · Thailand · United Kingdom

Preface

Polyimides have unique physicochemical properties: strong resistance to high temperature, radiation and chemical resistance, good mechanical strength, superior insulation properties, etc. These properties make polyimides valuable materials which can be used widely in different branches of industry. These properties have been well investigated and described in a series of monographs, and they continue to be studied quite actively.

The vigorous development of membrane science and technologies in the course of the last two decades has promoted evolution in the field of polyimide membranes. It was discovered that polyimides have excellent mass exchange characteristics, which together with the complex of their other physicochemical properties make them extraordinary materials for separation and purification technologies. The science and technology of polyimide membranes, as well as other kinds of membranes, are developing from the study of the mechanism of polymer synthesis, to include investigation of the polyimide mass exchange properties, the development of the technology of preparation and production of polymer membranes, and, finally, applications. Therefore massive information has been accumulated in the field of polyimide membranes, necessitating generalization and organization of this information. This is what led the authors to write this monograph. This volume is the first attempt to provide a general analysis of developments in the field, including polymer synthesis and leading to polymer membrane applications.

The authors collaborated to produce the book to demonstrate the high level of scientific research in Russia and the active development of applied research in Japan. Prof. V.V. Kudryavtsev, Institute of Macromolecular Compounds, Russian Academy of Sciences, has for many years investigated the basic rules of polyimide synthesis and is the author of a series of monographs on this problem. Dr. S.I. Semenova, Senior Researcher, Polimersintez, Russia (currently working at Yokohama National University), has for 20 years investigated the influence of the chemical structure of polymers on their mass transfer properties, and also helped developed technologies for membrane preparation. Prof. H. Ohya, Yokohama National University, is the leader of this team because he has been engaged in the research and development of membrane science for more than 25 years. Recently his interest has turned to membranes applicable to non-aqueous solutions and high temperatures, particularly supercritical fluids.

It is quite valuable, from our point of view, that the volume contains many references in Russian and Japanese. We hope that the reader will find this monograph and its bibliography a useful addition to the existing literature on polyimide membranes.

We are deeply indebted to Dr. V.I. Landysheva for her invaluable help in the statistical analysis of the patent information. We thank Ms. I.L. Turetskaya and Dr. Y. Hata for their help in collecting the information for this book. We also thank Mr. A.V. Malov for his participation in the translation of the work into English.

May 15, 1996

Haruhiko Ohya
Vladislav V. Kudryavtsev
Svetlana I. Semenova

Contents

1

Introduction. Trends in Polyimide Membrane Development

1.1 Advantages of Polyimides as Membrane Materials

Aromatic polyimides were first produced in 1908 by Marston Bogert through polycondensation of ethers or anhydride of 4-aminophthalic acid. In 1955 high molecular weight products were synthesized by two-stage polycondensation of pyromellitic dianhydride with diamines.[1] Since then, the interest of researchers in this class of polymers has been growing steadily because it possesses a number of valuable physico-mechanical and chemical properties. The superior thermal stability of polyimides was appreciated from very early on. Prolonged use of polyimides is possible at temperatures of up to 200° C, and short-term heating at temperatures of up to 480° C. Polyimides are nonflammable, stable at room temperature to organic solvents and concentrated acids (excluding sulfuric and nitric acids). Polyimides exhibit excellent physico-mechanical properties in a broad temperature range, exceptionally high radiation resistance and superior semiconductor properties. These characteristics predetermined the main polyimide applications in electronics, electrical engineering and aviation. The interest of researchers in the properties of polyimids is not declining. A number of monographs and surveys summing up the accumulated information have been published in recent years.[2–6] Valuable properties of polyimides discovered relatively recently include excellent mass exchange characteristics.

It is well known that in order to obtain polymers which exhibit both high gas selectivity and permeability it is necessary to synthesize structures with stiff backbone chains and with chain packing "calibrated" so as to produce a very narrow free-volume distribution. In other words, it is necessary to generate polymeric "molecular sieves." Polyimides are perfect materials for this purpose; their separation properties, particularly gas separation properties with respect to simple gases, are much better than other polymers and their rich potential has not yet been completely mined. The high rigidity of ensemble polyimide macromolecules and their suitable polarity plus the capability of forming hydrogen bonds explain why these polymers can be used also for separation of polar gases, vapors and liquids (e.g. water and organic substances). Polyimids are also prospective material for ultra- and microfiltration because of their high chemical resistance and wide possibility for modifications of membranes. The advantages of polyimide membranes for different functional purposes are due to high thermo- and chemical stability and excellent physico-mechanical properties.

1.2 Statistical Analysis of Patent Information Flows

As is well known, any achievement in engineering and technology becomes the object of scrutiny for inventors and can become a candidate for patent protection. The level of patenting activity can serve as an indicator of the development rate of a scientific-technical field. To discover general trends in the development of polyimide separation membranes, a retrospective analysis of a patent information corpus on the subject for the years 1962-1992 (year of publication) totaling about 200 patent documents was undertaken. This corpus of documents is a representative random sample on the subject of polyimide membranes. It is known that if a representative random sample of priority documents taken from an information corpus displays some regularity, then this regularity applies to the entire information corpus.[7] Thus by analyzing this sample it becomes possible to follow the character of inventorship development in the investigated field, to extent the revealed regularity to the whole collection of patents, and, consequently, the tehcnological development reflected in them.

Figure 1.1 shows the dynamics of yearly flows of patent information on polyimide separation membranes. It clearly has a pulsating character which is quite typical of patent information flows. It is noteworthy that the frequency of information outbursts has risen during the latest decade.

Almost all patents contain information on membrane preparation. Half of the patents specify methods of polymer synthesis as well as possible applications for the membranes. Only 5% of the corpus contains information on the use of polyimide membranes in units, modules and processes. The problem of polyimide membranes appears to be at the start of development where the very fact of membrane preparation, polymer synthesis and possible applications are of the greatest interest. High rates of information accumulation (see Fig. 1.2) are indicative of the high scientific potential of these issues.

Analysis of polyimide membranes application in various separation processes indicates that almost half (47%) of the total number of priority documents are concerned with gas

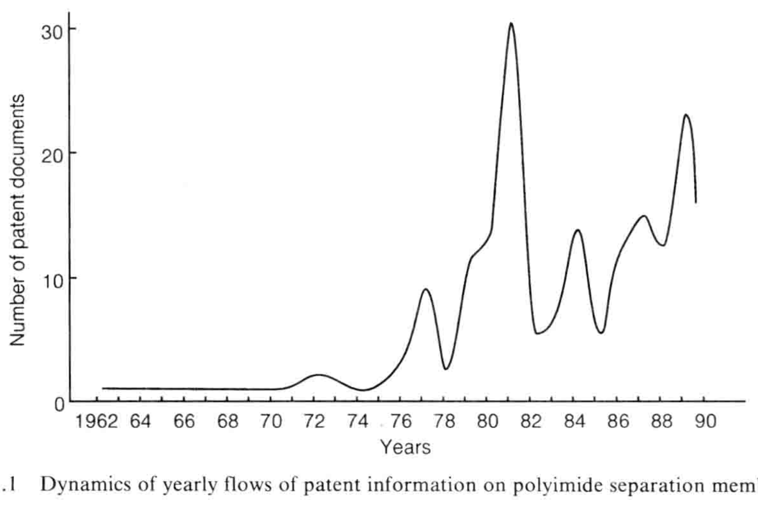


Fig. 1.1 Dynamics of yearly flows of patent information on polyimide separation membranes.

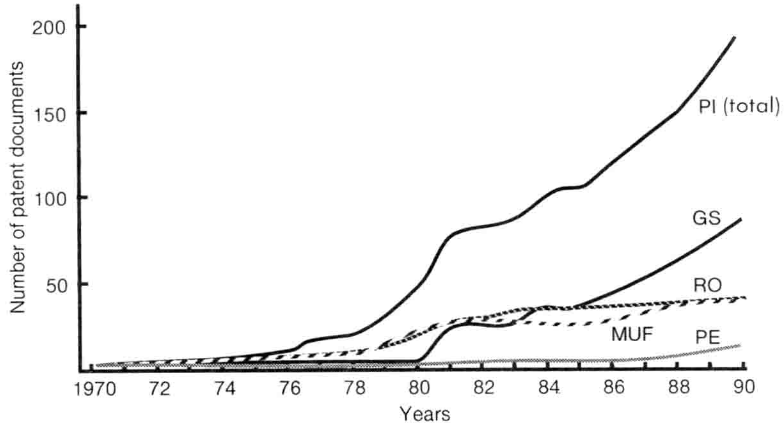


Fig. 1.2 Cumulative curves of patent information flows on polyimide separation membranes (PI), polyimide membranes in the processes of gas separation (GS), reverse osmosis (RO), micro- and ultrafiltration (MUF) and pervaporation (PE).

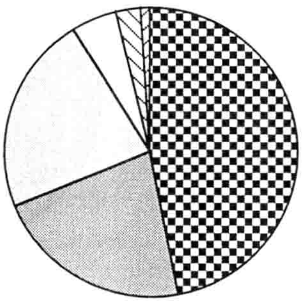
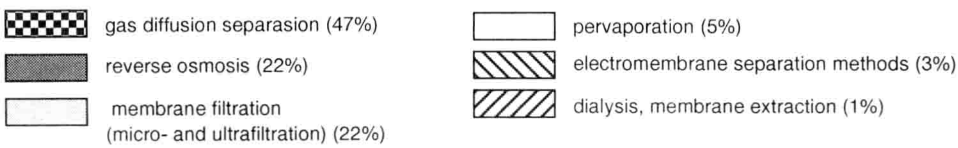


Fig. 1.3 Percentage of polyimide membrane application in various separation processes (based on analysis of polyimide separation membrane patent corpus).



diffusion separation. Among liquid separation methods, micro- and ultrafiltration (22% of the total number of priority documents) and reverse osmosis (22%) are dealt with most extensively. Application of polyimide membranes is reported in pervaporation (5%), electromembrane separation (3%), membrane extraction, and dialysis (1%) (see Fig. 1.3).

The highest patent activity in the field of polyimide separation membranes is displayed by scientists in Japan (55%), the USA (32%) and Germany (5%). They account for 92% of patent information on the subject in questions from 1970 to 1990 (see Fig. 1.4). This situation remains more or less the same at the present time.

The companies concerned with the problem of polyimide membranes and showing the highest patenting activity are listed in Table 1.1.

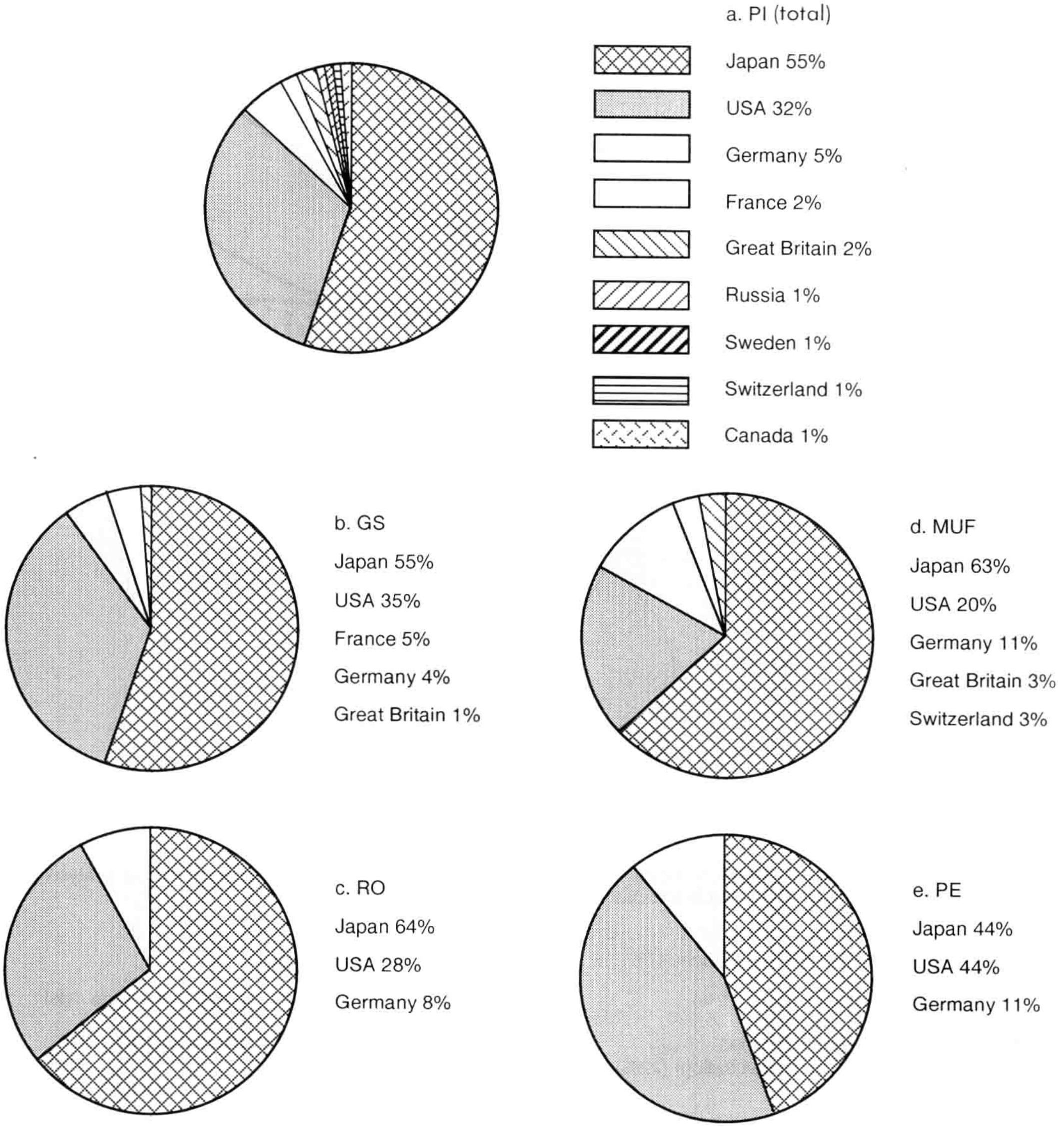


Fig. 1.4 Patenting activity of scientists of various countries (1970 – 1990):
a, Polyimide separation membranes (PI); b, Polyimide membranes for gas separation (GS); c, Polyimide membranes for reverse osmosis (RO); d, Polyimide membranes for micro- and ultrafiltration (MUF); e, Polyimide membranes for pervaporation (PE).

Table 1.1 List of the companies most active in patenting†

Problem	Country	Company	Percentage of priority documents
Polyimide separation membranes (total)	JP	Ube Ind. Ltd.	17
	JP	Nitto Electric Ind. Co. Ltd.	16
	US	E. I. Du Pont de Nemours and Co.	7
	US	Exxon Corp.	6
	JP	Mitsubishi Chemical Ind. Ltd.	3
		Other companies, including:	51
	FR	Institut Français du Pétrole	
	JP	Agency Industrial Science and Technology	
	US	Air Products and Chemicals Inc.	
	JP	Toybo Co. Ltd.	
	US	Bend Research Inc.	
	JP	Mitsubishi Rayon Co. Ltd.	
	JP	Teijin Ltd.	
	DE	Ges (GZS) fur Kernenergieverwertung in Schiffbau und Schiffahrt	
	US	The Dow Chemical Co.	
	GB	The British Petroleum (Co. Ltd.)	
Polyimide membranes for gas separation	JP	Ube Ind. Ltd.	31
	US	E. I. Du Pont de Nemours and Co.	13
	FR	Institut Français du Pétrole	5
	JP	Agency Industrial Science and Technology	5
	US	Air Products and Chemicals Inc.	5
	JP	Mitsubishi Rayon Co. Ltd.	5
	JP	Nitto Electric Ind. Co. Ltd.	4
	DE	Ges (GZS) fur Kernenergieverwertung in Schiffbau und Schiffahrt	4
		Other companies, including:	28
	US	The Dow Chemical Co.	
	JP	Shin-Etsu Chemical Company	
	US	Celanese Corp.	
	JP	Fuji Photo Film Co. Ltd.	
	GB	The British Petroleum (Co. Ltd.)	
	JP	Sumimoto Electric Inc. Co. Ltd.	
Polyimide membranes for reverse osmosis	JP	Ube Ind. Ltd.	22
	JP	Nitto Electric Ind. Co. Ltd.	17
	US	Exxon Corp.	14
	US	Bend Research Inc.	8
	JP	Teijin Ltd.	8
	JP	Toybo Co. Ltd.	6
	DE	Bayer AG	6
		Other companies, including:	19
	JP	Mitsubishi Rayon Co. Ltd.	
	US	USA Secretary of the Interior	
	US	Allied Chemical Corp.	
	JP	Toray Industries Inc.	
	JP	Chisso Corp.	
	JP	Asahi Glass Co. Ltd.	

(*Continued* on p. 6)

Table 1.1—*Continued*

Polyimide membranes for micro- and ultra-filtration	JP	Nitto Electric Ind. Co. Ltd.	35
	JP	Ube Ind. Ltd.	9
	JP	Mitsubishi Rayon Co. Ltd.	6
	DE	Bayer AG	6
		Other companies, including:	44
	US	Standard Oil	
	DE	Henkel KGaA	
	GB	Domnick Hunter Filters Ltd	
	DE	Ges (GZS) für Kernenergieverwertung in Schiffbau und Schiffahrt	
	US	Assignee Rohm and Hass Company	
	US	Raychem Corp.	
	US	Gelman Instrument Co.	
	US	Celanese Corp.	
	US	Exxon Corp.	
	US	Allied Chemical Corp.	
	JP	Toybo Co. Ltd.	
	JP	Toray Industries Inc.	
Polyimide membranes for pervaporation	US	Exxon Corp.	44
	JP	Toybo Co. Ltd.	22
	JP	Ube Ind. Ltd.	11
	JP	Sagami Chemical Research Center	11
		Other companies	12

† These companies issued priority documents from 1970 to 1990 on various aspects of polyimide membranes. The percentage of priority documents is their contribution to the respective patent corpuses.

1.3 The First Steps in Commercial Application of Polyimide Membrane

S.I. Du Pont De Nemours and Co. (USA) and Ube Industries (Japan) are pioneers in the commercial application of polyimides in separation processes.

The development of membranes for industrial separations by DuPont began in 1962 with the initial concept of separating helium from natural gas. Although the first industrial application of this pioneering work was DuPont's Permasep® reverse osmosis system for purifying and desalinating water (introduced in 1970) this work established the technological foundation for gas separations. Over the last quarter-century this technology has advanced significantly to keep pace with changing and expanding market needs and a rapidly moving competitive environment.

One of the major types of polymer membrane materials being manufactured by DuPont is Kapton produced by polycondensation of pyromellite dianhydride and 4,4′-diaminodiphenyl ether.

New polymers that exhibit a unique combination of flux and selectivity well suited for a variety of commercial applications have been developed and converted to membranes.

The first commercial application of this technology was in 1987 at Conoco's Ponca City, Oklahoma, refinery for the recovery of hydrogen from a hydrotreater purge stream. This system processes 12 million standard cubic feet per day of refinery gas through three 10-ft long, 12-in diameter permeators. The system has operated successfully for over two years. The membrane is a polyamide hollow fiber. Membrane systems based on new polyimides and novel membrane-formation technology have been developed for producing 90 – 99+% N_2 from air at high productivity and recovery. This represents a breakthrough and is expected to expand the market for membranes over competitive technologies. Several systems are already in operation, including the world's largest capacity membrane-nitrogen system. This technology is also being tested on a pilot scale for the separation of CO_2 from various gas streams.

Ube Industries started investigating aromatic polyimide as a membrane material in April 1978. The company took part in the C_1 Chemistry Large-Scale Project in Japan, which started in FY 1980 and was completed in December 1986. Development of polyimide membranes and modules based on the membranes is one the results of Ube Industries' activities within the framework of C_1.[8)]

In 1981 Ube Industries developed and launched the production of the Upilex-R polyimide material, which exhibits high heat and thermal resistance and stability to various organic solvents and vapors as well as hydrogen sulphide and ammonia vapors. Upilex-R is produced by polycondensation of 3,3′,4,4′-biphenyltetracarboxylic dianhydride and 4,4′-diaminodiphenyl ether. In 1986 a pilot plant was launched for recovery of H_2 from synthesis gas in ammonia production, using polyimide membranes in the form of asymmetric hollow fibers. The membranes have admissible operating temperature of up to 150°C and are capable of withstanding feed flux pressures of several tens of atmospheres. Membrane units using Ube Industries' hollow fiber polyimide membranes are effectively competing with Monsanto units using hollow fiber polysulphone membranes in hydrogen recovery processes.

Thus the flow of periodic and patent information on polyimide membranes has now become strong enough to necessitate and enable generalization of the accumulated information. Moreover, commercial applications of polyimide membranes are growing rapidly, leading to the authors' decision to write this volume.

The present monograph discusses issues related to the synthesis of polyimides as materials for membranes. Discussed rather briefly are structure-properties relationships of polyimides such as peculiarities of conformations of polyimide macromolecules and dependence of main transition points on chemical structure. A brief discussion of these sufficiently well studied issues is required because the enumerated properties determine to a large extent mass-exchange characteristics of polyimides. Close attention is paid to the effect of the chemical structure of polyimides on their mass-exchange properties. The major methods of polyimide membrane preparation described in the literature are considered. Examples of commercial applications of polyimide membranes are given.

Chapter 2 on synthesis and chemical structure of polyimides was written by Professor V. Kudryavtsev, Institute of Macromolecular Compounds, Russian Academy of Science; the Introduction, Chapter 3 "Structure-Properties Relationships of Polyimides", Chapter 4 "Separation Properties of Polyimides," and Chapter 5 "Preparation of Polyimide Membranes," were written by Dr. S. Semenova, Senior Researcher, Polimersintez, Russia (currently working at Yokohama National University); Chapter 6 "Industrial Applicaition of Polyimide Membranes," was written by Professor H. Ohya, Yokohama Naitonal University.

The authors hope that the reader will find the book and its bibliography a useful addition to the existing literature on polyimide membranes.

References

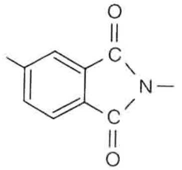
1. Bühler, K.U., *Spezialplaste,* Chapt. 7.11.1, Academie-Verlag, Berlin, 1978 (in German).
2. Bessonov, M.I., Koton, M.M., Kudryavtsev, V.V., and Laius, A.A., *Polyimides, A Class of Thermostable Polymer,* Bessonov, M.E., ed., Leningrad, Nauka, 1983 (in Russian).
3. Mittal, K.L., ed., *Polyimides: Synthesis, Characterization and Application,* Vol. 1, Vol. 2, Plenum Press, N.Y., 1984.
4. Bessonov, M.I., Koton M.M., Kudryavtsev V.V., and Laius L.A., *Polyimides: Thermally Stable Polymers,* Plenum Press, N.Y., 1987.
5. Bessonov, M.I., and Zubkov V.A., ed., *Polyamic Acids and Polyimides. Synthesis, Tranformations, and Structure.* CRC Press, Boca Raton, Ann Arbor, London, Tokyo, 1993.
6. Sroog, C.E., *Prog. Polym. Sci.,* **16**, 561 – 694, 1991.
7. Landysheva, V.A., Shinyayev, L.I., Soldatova, A.F., and Modina, Z.V., *Plastmassy,* No. 9, pp. 54 – 56, 1986 (in Russian).
8. Ubersax, R.W., Proc. Int. Congr. on Membranes and Membrane Proc. ICOM'90, Chicago, USA, **1**, 798 – 799, 1990.

2

Synthesis of Polyimides

2.1 Basic Rules of the Polycondensation Process of Polyamic Acid Formation

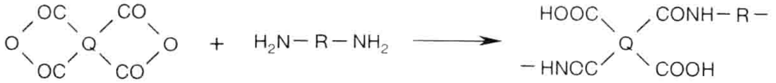
Generally, the term "polyimides" refers to heterochain polymers containing an imide (benzimide) group on the backbone:



The literature on the formation reactions and properties of polyimides is vast.[1-5] Depending on the chemical nature of the imide (benzimide) cycle, the basic techniques for polyimide production rely on reactions of diamine polyacylation by tetracarboxylic acid derivatives where the reactions of polyacylation of aromatic and heterocylic diamines by dianhydrides of aromatic, alicyclic and aliphatic tetracarboxylic acids are of the greatest practical value.

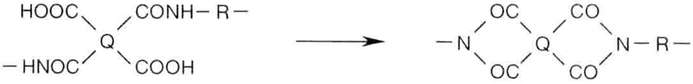
Diamine polyacylation by dianhydrides can be carried out in one or two stages. If the final polyimides are to be insoluble in organic solvents, two-stage synthesis of polyimides with intermediate formation of polyamic acids is carried out. The two-stage synthesis has the following reaction scheme.

First stage:



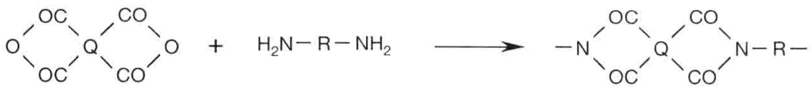
where Q is residue (radical) of tetracarboxylic acid and R is residue (radical) of aromatic diamine.

Second stage:



The solutions of polyamic acids produced at the first stage of synthesis are used to cast various products (films, fibers, coatings, molding powder, etc.). The second stage of synthesis, called imidization, is carried out in cast products by thermal treatment of polyamic acids or by treating polyamic acids with water-capturing agents in the presence of catalysts. By using the two-stage synthesis scheme, diverse products can be made from insoluble non-fusible polyimides.

If, on the contrary, the final polyimides are to be soluble in phenol or other organic solvents, one-stage synthesis of polyimides is carried out according to the following reaction scheme:



Both two-stage and one-stage techniques of polyimide synthesis are important for production of polyimide membranes. Chemical conversions and physical phenomena taking place during two-stage synthesis are discussed in more detail in the scientific literature compared to one-stage synthesis of polyimides. When discussing two-stage synthesis of polyimides we do not intend to provide a historical sketch of the problem or to systematically describe numerous available factual data. This has been discussed extensively in surveys and monographs.[1-8] We intend to cover relatively unknown results of research on the kinetics of formation and degradation of polyamic acids as well as the effect of several factors on properties of polyamic acids in solutions necessary for the proper control of polycondensation processes in the synthesis of polyimides.

2.1.1 Quantitative Characterization of the Polycondensation Process of Aromatic Dianhydrides with Aromatic Diamines

On the face of it, polyamic acid production processes look quite simple. Tetracarboxylic acid dianhydride powder is added portionwise, say in two doses, under stirring, to an aromatic diamine solution in a suitable solvent (dimethylformamide, dimethylacetamide, methylpyrrolidone, diglyme, etc.). Depending on the selected dianhydride and diamine, the viscosity of the solution can increase either in a landslide manner up to several dozens of poise, or can build up over several hours. If the intention is to produce high MW polyamic acid, then preliminary dissolution of dianhydride is not employed and the order of reactant addition is not changed, *i.e.* diamine or its solution is not introduced into the dianhydride solution. Temperature of the reaction solution is maintained within 15° to 35°C. In the synthesis of polyamic acids in reactors having a volume of more than 1 liter, heat pick-up should be provided. Concentration of the reactant solution is selected depending on the end use of the polyamic acid; it should be borne in mind that concentration is an efficient means of control over the molecular weight of the polyamic acid. Concentration of the polyamic acid solution is normally 8 to 18% by weight. In the synthesis of polyamic acids slight deviations from the stoichiometric proportion of reactants are admissible, small deviations from stoichiometry strongly affecting the molecular weight of polyamic acids. Solutions of polyamic acids are instable even at room temperature, the instability being of a spontaneous nature. Polyamic acids should be stored at no more than 0°C.

At present several dozen dianhydrides and even more diamines are used in the synthesis