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FINAL REPORT  
UNDER CONTRACT NO. 84/95

UNIDO PROJECT NO. DP/YUG/82/005  
ACTIVITY CODE: DP/94/32.1

Polymer Technologies, Inc.  
(Formerly Polymer Institute)  
University of Detroit  
Detroit, Michigan 48221

November, 1986

Dr. K.C. Frisch  
Dr. D. Klempner

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## 1. INTRODUCTION

The Polymer Institute, University of Detroit, on the basis of contract No. 84/95 between the United Nations Industrial Development Organization (UNIDO) and the Polymer Institute, assisted the Yugoslav Government as a consulting company in realizing the objective of the project: DP/YUG/82/005 "Development of Polyether Synthesis and Processing Technology for Polyurethanes and Other Industrial Applications."

The development objective of this project was the establishment and expansion of plastic applications in the selected sub-sectors of industry, i.e. in engineering, automotive, furniture, building industries and domestic appliances, through the use of modern and further elaboration of locally applicable technologies with the aim of enabling a continuing contribution to the economic development of the country.

The project has two main immediate objectives:

A. Development of environmentally-safe technologies with optimal domestic application for the production of diversified polyethers and their application in the industrial production of various types of polyurethanes, synthetic lubricating fluids and cosmetic products.

B. Strengthening of the existing polymer research and testing laboratories at the SODASO Institute to provide industry with an independent source of advice and assistance in the field of polyethers production and their further application in various

industries. This objective was anticipated to be achieved by:

- Improving the ability of the staff at the SODASO Institute to carry out research and development work in the field of polyethers and polyurethane synthesis and processing.
- Establishing the capability of SODASO Institute for the development of new national standards and the supplementation of the existing ones.
- Upgrading of the graduate and post-graduate courses by the inclusion of the polyethers-polyurethanes course content into the syllabus and also the introduction of the short term courses for the industry personnel.
- Establishing technical information service appropriate to the needs of the industry for polyether-polyurethane applications.

The Polymer Institute trained the SODASO Institute's personnel in different fields of polyether and polyurethane chemistry and technology, including polyurethane production technology, the use of equipment for the production of polyurethanes, characterization of physico-chemical properties of the raw materials and intermediates, monitoring physico-mechanical properties of the finished polyurethane products and their further application as materials in other sectors of industry. The Polymer Institute also provided training in the field of environmental precautions, occupational health and consumer's health risks (i.e. safety aspects). Special assistance was provided in the development of the scientific research work in the field of polyurethanes through the joint research work which was partly carried out in Yugoslavia, in view of the modest equipment available at SODASO Institute, and on the premises of the Polymer Institute itself through the direct work of the SODASO Institute staff at the Polymer Institute in Detroit.

The following is a summary of the Polymer Institute's activities.

- Organized and carried out the training of 13 members of the SODASO Institute staff, in various fields of polyurethanes including polyurethane foams, micro-cellular polyurethane elastomers, polyurethane coatings and adhesives, polyurethane thermoplastic and cast elastomers and the marketing of polyurethanes.
- Four visits by experts from the Polymer Institute were made to SODASO Institute in Yugoslavia.
- Assisted in the programming of research and the development of polyether polyols and polyurethane systems for rigid self-extinguishing foams (this program was carried out in Yugoslavia).
- Participated in the programming and realization of joint research projects in the field of thermally stable polyisocyanate polymers based on oxazolidone, and in the field of catalysis, kinetics and mechanism of the cyclotrimerization of isocyanates (the joint research projects were carried out in Yugoslavia and the U.S.A.).
- Assisted in establishing an international "School of Polyurethanes" (workshop) in Tuzla, Yugoslavia (the fourth "School" will be held from September 1-6, 1986).
- Assisted in the preparation of the thematic issue of the journal "Polimeri" in the field of polyurethanes (Vol. 7, No. 6-7, 1986).

The immediate results of the activities of the Polymer Institute, in the implementation of the Contract No. 84/95, between UNIDO and the Polymer Institute, University of Detroit, are as follows:

- Thirteen members of SODASO Institute, Tuzla, Yugoslavia, were trained to independently design and conduct research and development in certain fields in polyurethanes. (See Table I for a list of trainees, programs, and periods of participation.) Professional papers and other information were published in the journal "Polimeri" in 1986 by the members of SODASO Institute who were trained at the Polymer Institute in Detroit. The members of SODASO Institute who were trained at the Polymer Institute represent approximately two-thirds of those employed at the Institute of Polyurethanes which has been formed as a new department of SODASO Institute in Tuzla.

- In certain fields of application, through training and research, members of the SODASO Institute developed formulations of polyurethane elastomers, coatings and adhesives, and formulations of polyether polyols and polyurethane systems for rigid self-extinguishing foams, which are already applied in production or are being introduced into production in Yugoslavia.
- On the basis of an in-depth study of catalysis, kinetics and mechanisms of the cyclotrimerization of isocyanates on model reactions (the joint research project) three members of SODASO Institute mastered the synthesis of thermally stable polyisocyanate polymers based on isocyanurate. One scientific paper has been submitted to the Journal of Polymer Science.
- On the basis of an indepth study of catalysis, kinetics and mechanisms of the synthesis of 2-oxazolidones (the joint research project) a new catalyst and original formulations of thermally stable coatings and thermally stable elastomers were developed. One patent application has been submitted (YUG Pat. Application P-2031/85, December, 1985). Two scientific papers are in press: in the journal "Polimeri" and the Journal of Polymer Science, Chemical Edition. Three scientific papers are in the preparation stage and will be submitted to the publishers this year. A member of the SODASO Institute defended their Ph.D. dissertation in the field of the joint research paper.
- The international "School of Polyurethanes" (workshop) was established in Tuzla on a permanent basis as a good base for organizing a UNIDO Group Training Program in Polyurethanes for industry in Yugoslavia and developing countries.
- Through the joint research projects a research group has been formed at the SODASO Institute for independent scientific research in the field of polyurethanes of which three members are lecturers at the IV School of Polyurethanes.

## II. BACKGROUND AND INFORMATION

### A. Polyurethane Production in Yugoslavia

Polyurethane production in Yugoslavia began in 1960 with flexible foams for the furniture industry. The present rate of production is 60,000 tons annually of various polyurethane products, which is dominated by:

- a. Flexible foams for the furniture industry, automotive industry, and transportation industry, in general.
- b. Production of rigid foams as structural and insulating materials for use in construction, home appliances and refrigeration.
- c. Micro-cellular elastomers for the footwear and automotive industry.

In addition, polyurethanes are used as coatings (particularly in the production of synthetic leather), elastomers, adhesives and sealants.

The polyurethane industry in Yugoslavia is equipped with modern equipment which has larger production capacity than is presently utilized.

Until 1976, the production of polyurethanes in Yugoslavia was entirely dependent upon imported raw materials, when the production of polyether polyols began (at a capacity 20,000 tons annually). Production of toluene diisocyanate (TDI) at a capacity of 18,000 tons annually began in 1984 and also under construction is a new capacity (ca. 18,000 tons annually) of TDI in Yugoslavia.

Assessing the real need for further industrial development in Yugoslavia, the Government Authorities concerned therefore decided to embark on a development program for the production of polyurethane raw materials and five years earlier started with the establishment of laboratories at SODASO Institute and equipped them for the physico-mechanical testing of polyurethanes.

With the aim of establishing the ability for the performance of semi-industrial testing, a pilot reactor for the production of polyethers was put into operation in 1985.



Through the financial support of the Yugoslav government and industry, and through the UN project (UNDP/UNIDO DP/YUG/82/005), the laboratories of the SODASO Institute have been equipped to that level where more complex testing and research can be carried out in polyurethane chemistry and technology. Through the training at the Polymer Institute in Detroit and through the joint research projects with the Polymer Institute, SODASO staff have been trained to independently program development and carry out research in the field of polyurethanes. This has resulted in the establishment of the Institute for Polyurethanes as a new department of the SODASO Institute. The Institute for Polyurethanes is qualified to carry out technical service and training of the staff of Yugoslav industry and developing countries.

However, it should be kept in mind that the production of polyurethanes is in a state of constant development, mainly because of market pressures for new and more sophisticated products, which are at the same time less expensive. This allows for a quick development of applications of an ever broadening base of raw materials for polyurethanes and a rapid development of new materials (composites, alloys, IPNS) and processes (RIM and RRIM). Therefore, it is necessary to maintain continuing education of the staff and keep laboratories well equipped at the Institute for Polyurethanes. This will enable long term development of polyurethanes in Yugoslavia, on which the entire development of the industry is dependent.

The establishment of the School of Polyurethanes in Tuzla made possible the direct contact and exchange of experience with

experts from developed countries. The School of Polyurethanes offers the opportunity for a high professional level of training and education for those in industry.

### III. RESULTS OF IMPLEMENTATION OF CONTRACT NO. 84/95

#### A. Training Program

Training of the Yugoslav staff (SODASO Institute) began November 1, 1984 and was completed according to the program defined in cooperation with the National Board of project DP/YUG/82/005, and in accordance with the contract No. 84/95 between UNIDO and the Polymer Institute, University of Detroit. The training program was prepared therefore to enable the personnel of SODASO Institute to independently develop diversified polyurethanes and their applications in various industrial production. Care was taken to insure safe technologies with optimal domestic (Yugoslav) application. An additional goal was to be able to provide industry with an independent source of advice and assistance in the field of polyurethane production and application in various industries.

The program of training entailed marketing of polyurethanes and the main fields of polyurethane production including polyurethane foams, microcellular polyurethane elastomers, polyurethane cast and thermoplastic elastomers, polyurethane coatings and polyurethane adhesives.

Each trainee was assigned to a senior staff member from the Polymer Institute. Dr. K.C. Frisch supervised the overall program. Laboratory space and equipment were provided for the

trainees to allow them to participate in the experimental work themselves. The basic chemistry of polyurethanes was reviewed, and the specific information concerning particular applications was discussed. Applications using polyether polyols and TDI were stressed since Yugoslavia manufactures these materials. The data on raw materials, typical formulations for each application, and procedures of standard testing methods were provided. Instructions on sample preparation and the operation of testing and characterization equipment were also given. The library at the University of Detroit was also made available for the trainees to do their literature search for new developments in their respective fields. In addition, special technical books on various phases of urethane technology, market reports, and technical data sheets from many industrial companies were also made available.

After the trainees had developed their skills by practicing with the conventional formulations, they proceeded to study the structure-property relationships of polyurethanes using different raw materials, such as diisocyanates, polyether and polyester polyols, and chain extenders, at various ratios of soft- and hard segments. The physical-mechanical properties of these prepared samples were measured.

A list of equipment and instrumentation available at the Polymer Institute is shown in Table II. This allows virtually complete testing of all the basic properties of all types of polyurethanes (foams, elastomers, coatings, adhesives, etc.) as well as characterization of the polyurethanes to allow

elucidation of structure-property relationships. In addition to measuring the polymers, this equipment also allows testing of all the raw materials utilized in polyurethanes. The trainees all had opportunities to use this equipment and to become familiar with all the basic measurements.

During the training special attention was given to insure that the counter part staff received appropriate training in the field of environment precaution, occupational health and consumer's health risks. A series of lectures was held and the trainees were supplied with the basic literature from this field. During experimental work the supervisors made sure that the trainees strictly adhered to the use of safety equipment.

So that the trainees would receive a broad knowledge from formulation, synthesis and testing of products to the technology, process equipment and application of the products, visits were organized to industrial research laboratories and production facilities. Also, a certain number of trainees visited other universities and scientific institutions and participated in several professional and scientific meetings in the U.S. The trainees visited the following companies and scientific institutions:

Several Persons	Dow Chemical Co. BASF Wyandotte Ford Motor Co. General Motors Corp. B.F. Goodrich	several trips
Dragan Brkich	Witco Upjohn Polaroid Polytechnic Institute of New York Massachusetts Institute of Technology Columbia University Harvard University SPI Headquarters, New York Union Carbide, New Jersey International Isocyanate Institute University of Massachusetts	3/25 - 4/1/85

The trainees participated in the following meetings:

Several Persons	SPI Meeting, Detroit	Feb. 1985
Aisa & Vahid Sendijarevic	SPI Meeting, Detroit	Feb. 1986
Aisa & Vahid Sendijarevic	Gordon Conference on Foams	Aug. 3-8, 1986
Jasminko Arnautovic	National Plastics Exhibition Polyurethane Manufacturers Association Meeting	4/21 - 4/24/85

The individual training programs are described below:

1. Polyurethane Adhesives

Trainee: Marija Vranes  
Duration: 3 months (Nov. 1, 1984 - Jan. 31, 1985)  
Advisor: Dr. D. Klempner

Thermosetting adhesives of polyurethane based on tolylene diisocyanate (TDI) and polyether polyols were studied. Prepolymers of TDI and poly(oxypropylene) glycol (different molecular weights, Pluracol P series, BASF Wyandotte) at various NCO/OH ratios were prepared. The concentration of free TDI in the prepolymer was determined by means of high performance liquid chromatography (HPLC). Methanol capped TDI was synthesized and used as a standard to determine the retention time and the correlation between the peak height and its concentration.

The adhesives were applied on both aluminum and steel panels. Peel strength (T-peel) and lap shear strength of these samples were measured according to ASTM methods D-1876 and D-1002. These provide the basic measures of adhesive strength.

## 2. Polyurethane Coatings

- A. Trainee: Mediha Ahmetovic  
Duration: 6 months (Nov. 1, 1984 - Jan. 31, 1985 &  
April 1, 1986 - June 30, 1986)  
Advisors: Drs. H.X. Xiao and S. Wong

During her first visit, polyurethane coatings were prepared using tolylene diisocyanate (TDI), poly(oxypropylene) glycols (PPG polyols at various molecular weights) and 4,4'-methyl bis(o-chloroaniline) (MOCA). The systems studied included one-component moisture cured (prepolymer of TDI/PPG polyol), and two-component polyether-based coatings (prepolymer of TDI/PPG polyol chain-extended with MOCA). Solvents such as toluene, xylene and cellosolve acetate were incorporated into the system either alone or in blends. The coatings were applied on steel and glass panels, and on polypropylene sheets to prepare free films. The following tests were performed on these films:

1. Drying time - finger touch method
2. Hardness  
scratch hardness - pencil method ASTM D 3363  
pendulum hardness - Sward hardness rocker
3. Bending test (elongation)  
Conical Mandrel Method ASTM D 1737
4. Tensile strength on free films ASTM D 638  
Instron tensile testing instrument on dumbbell-shaped specimen
5. Impact resistance - Gardner impact tester -  
direct and indirect
6. Abrasion resistance - rotating disc abrasion tester
7. Resistance to solvents

Oligomers of isocyanurate containing TDI were successfully prepared. HPLC analysis on the methanol capped oligomer showed no free TDI remaining in the solution. Films were made from this TDI oligomer and PPG based polyols.

During her second visit to the Polymer Institute, Ms. Ahmetovic concentrated her studies on the modification of TDI

by partial capping with trimethylolpropane (TMP) and preparing oligomers. The content of monomeric TDI was determined by high performance liquid chromatography (HPLC).

- B. Trainee: Hajrija Sehovic  
Duration: 3 months (April 1, 1986 - July 8, 1986)  
Advisor: Dr. S. Wong

One component coatings based on the prepolymers of different diisocyanates (MDI, TDI, HMDI and  $H_{12}$ MDI) and polyether polyols (PTMG at different molecular weights) and epoxide (diglycidyl ether of bisphenol A- DER 332) were synthesized in solvents using the 2-oxazolidone catalysts (LiCl, LiCl/HMPA and  $AlCl_3$ /TPPO). The effects of the structure of diisocyanates, the molecular weight of the polyols, the catalysts, and the concentration of 2-oxazolidone on the resulting films were evaluated. Characterization of the formation of urethane and 2-oxazolidone linkages was determined by means of FTIR. The properties (free film and the coated Al-, steel panels) tested were pencil hardness, Gardner impact (direct & reverse), tensile strength, elongation, and TGA. The results of this study (in preparation) will be published in a scientific journal (J. of Coatings Technology).

### 3. Polyurethane Elastomers

- A. Trainee: Ivan Javni  
Duration: 2 months (Nov. 1, 1984 - Jan. 5, 1985)  
Advisor: Dr. S. Wong

Segmented polyurethane elastomers were prepared by the prepolymer method (two-step process). Prepolymers were based on 4,4'-methylene diphenyl isocyanate (MDI) and two polyether polyols [poly(oxytetramethylene) glycol, Teracol 1000, Du Pont and

poly(oxypropylene) glycol, Pluracol P1010, BASF-Wyandotte] and one polyester polyol [polycaprolactone polyol, Tone polyol L-0220, Union Carbide] of molecular weight approximately 1000 at an NCO/OH ratio of 3/1. Testing sheets and buttons were prepared by chain-extending the prepolymers with 1,4-butanediol. The isocyanate indices of these elastomers were kept at 105. The effect of tin-catalyst (dibutyltin dilaurate) on the gelation of the polymers was studied. The following tests were performed:

1. Viscosity of prepolymer - Brookfield viscometer
2. Shore hardness, ASTM D 2240  
Shore A  
Shore D
3. Stress-strain properties, ASTM D 412  
secant modulus at various elongations  
tensile strength  
elongation  
elongation set
4. Tear resistance  
Graves die C, ASTM D 624  
Split tear, ASTM D 1933
5. Resilience, ASTM D 2632
6. Compression strength, ASTM D 575
7. Compression set, ASTM D 395

B. Trainee: Radojka Dobrosavljevic  
Duration: 3 months (April 1, 1985 - June 30, 1985)  
Advisor: Dr. S. Wong

The synthetic procedures and testing methods of this program were about the same as described previously in section A. The effects of molecular weight of polyether polyol and chain extender of the TDI-based polyurethane elastomers were studied. Poly(oxypropylene) glycols of four different molecular weights (Pluracol P2010, 1010, 710 and 410), and amine chain extender, 4,4'-methylene bis(o-chloroaniline) (MOCA) and two short chain diols, 1,4-butanediol and hydroquinone di-( $\beta$ -hydroxyethyl) ether (HQEE) were employed. The mechanical properties of these elastomers were evaluated as in A above.



C. Trainee: Mevlida Vlajic  
Duration: 3½ months (April 1, 1986 - July 15, 1986)  
Supervisor: Dr. S. Wong

Segmented polyurethane elastomers were prepared by the prepolymer method (two step process). Prepolymers were based on MDI and TDI and two polyether polyols (PTMG and PPG with different molecular weights) and two polyester polyols (Tone and adipate ester at molecular weight of 1000) at various NCO/OH ratios. The chain extenders used were 1,4BD, HQEE, 1,3 propane-diol, TMP and 1,6-hexanediol. The following physical properties from the resulting test sheets were determined:

1. Shore hardness, ASTM D 2240  
Shore A  
Shore D
2. Stress-strain properties, ASTM D 412  
secant modulus at various elongations  
tensile strength  
elongation  
elongation set
3. Tear resistance  
Graves die C, ASTM D 624  
Split tear, ASTM D 1983

D. Trainees: Aisa Sendijarevic  
Vahid Sendijarevic

Duration: 6 months (Feb. 15, 1986 - Aug. 13, 1986)  
Advisor: Dr. K.C. Frisch

2-oxazolidone-containing polyurethane elastomers were synthesized using different diisocyanates, polyether polyols and epoxides. Catalysts used were LiCl, MgCl<sub>2</sub>/HMPA and AlCl<sub>3</sub>/HMPA. The elastomers were cast-cured at 150°C. The hardness, stress-strain properties and tear resistance of these elastomers along with their thermal stability (TGA) were evaluated. Due to the time limitation, this work will be continued in Yugoslavia.

#### 4. Polyurethane Foams

Trainee: Irfan Busuladovic  
Duration: 3 months (Feb. 1, 1985 - April 30, 1985)  
Advisor: Dr. J.E. Kresta

The training was started with a literature survey of the preparation of flame retardancy characterization and testing of rigid urethane foams.

In the experimental training, rigid urethane foams were prepared using polymeric isocyanates, polyether polyols of high functionality, various amine catalysts and surfactants. The density was varied by using different amounts of blowing agents (physical-Freon 11A; chemical-H<sub>2</sub>O). The relationship between the foam density and foam properties (compression strength and friability) was investigated. The effects of various flame retardants (containing P and Cl) and their concentration on the flammability of the rigid urethane foams were evaluated.

The prepared urethane rigid foams were tested according to the following ASTM test methods:

Density	ASTM D 1622
Friability	ASTM D 421
Oxygen Index	ASTM D 2863
Flammability	ASTM D 3014
Compressive Strength	ASTM D 1629

#### 5. Polyurethane Microcellular Elastomers

Trainee: Bozo Banjanin  
Duration: 6 months (April 1, 1985 - Sept. 30, 1985)  
Advisor: Dr. K. Ashida

Microcellular foams have been used in the shoe-sole industry, automotive interior parts, e.g. glove box lids, steering wheels, etc.

This training was started with a literature survey on preparation, characterization and application of microcellular

elastomers. Copies of different testing methods have been collected.

Experimental training started by using a liquefied MDI (Isonate 143L, Upjohn Company) and different types of polyether polyols.

TDI-based microcellular elastomers will be investigated after the evaluation of the MDI-based microcellular elastomers has been finished.

#### 6. Marketing

Trainees: Dragan Brkic  
Jusuf Suljkanovic  
Jasminko Arnautovic  
Duration: 2-6 months  
Advisors: Entire staff

All of the staff members of the Polymer Institute took part in the training of the marketing group. Lectures and discussions were held. Much marketing information - literature was supplied to each trainee, and numerous trips to companies and plastic shows were made. At these trips (which the technical trainees also attended), the trainees had opportunities to discuss marketing with the company representatives as well as see the polyurethane laboratories and production facilities. Companies visited included BASF-Wyandotte, Witco, Ford Motor Company, B.F. Goodrich, General Motors Corp., Upjohn and Polaroid. In addition, they attended several meetings including the National Plastics Exhibition in Chicago and the Polyurethane Manufacturers Association meeting in Callaway Gardens near Atlanta, Georgia. They also visited a number of universities and organizations, including the Polytechnic Institute of New York, Massachusetts Institute of Technology (MIT), Columbia, Harvard as well as the headquarters of the Society of the Plastics Industry in New York City.

## B. Joint Research

In recent years the standards for thermal stability of polymer materials, including polyurethanes, have become more rigorous. The U.S., Japan and other developed countries have defined by law very rigorous regulations for the fire performance of polymers and it is only a matter of time before the same resolution will be made by the Yugoslav government. Therefore, in the further development of production and application of polyurethanes, thermal stability will play an important role. Because of this, research in thermal stability of polyurethanes has been given special attention. In scientific and professional publications, and in the newest commercial polyurethane products of the leading producers of polyurethanes in the world, the classic polyurethane structure has been modified and polymers based on polyisocyanates are becoming more popular.

Yugoslavia is a producer of the basic raw materials for polyurethanes (polyether polyols and TDI) and polyurethane systems. By putting into production a new capacity of TDI, Yugoslavia will have a total production of approximately 36,000 tons of this type of isocyanate with limited demand on the domestic market for the production of flexible foams (ca 7,000 tons annually). A possible solution for the development of the domestic market of TDI is substitution of other isocyanates by the production of polyisocyanate based polymers (polyisocyanurate and polyoxazolidone based polymers and copolymers) for applications in the production of rigid foams, coatings,

sealants, elastomers. etc.

The joint research projects included research on the synthesis of polyisocyanate polymers and copolymers of isocyanurate and oxazolidone. Catalysis, kinetics and mechanisms of these reactions were studied on model compounds. The structure-property relationships were also studied. As a result of this joint research a new catalyst for low temperature synthesis of oxazolidones in solvents was developed and thermally stable (more than 100°C more stable than polyurethanes) coatings and elastomers were also developed. The SODASO staff is capable of independently carrying out the development of these types of polymers and in other fields of applications such as foams, microcellular elastomers and sealants. In the joint research, which was carried out in Tuzla and Detroit, the following SODASO staff members participated:

1. Dr. Vahid Sendijarevic
2. Dr. Aisa Sendijarevic
3. Hajrija Sehovic
4. Mirjana Zilic

The joint research resulted in publications. One member of the SODASO staff (Aisa Sendijarevic) defended her Ph.D. dissertation in the field of the joint research, and another Ph.D. dissertation (Hajrija Sehovic) and one masters thesis (Mirjana Zilic) are also in the preparation phase.

As a result of the joint research, the SODASO staff is capable of independent planning of scientific projects in the field of polyurethanes.

### C. Other Activities

Along with the organization of the program for the training and joint research projects, the Polymer Institute

assisted members of the SODASO Institute, through the visits of staff from the Polymer Institute, with the programming of research and development in the production of polyether polyols and polyurethane systems for self-extinguishing rigid foams. In the production line of TDI at the SODASO Chloralkali Complex in Tuzla one of the intermediates is toluene diamine (TDA) which is an excellent initiator in the synthesis of polyether polyols. Polyurethanes obtained from polyether polyols from TDA as initiator, because of the presence of an aromatic structure, have a far greater thermal stability and fire performance in relation to other types of polyether polyols. Therefore, production of these types of polyols represents a larger portion of the total production of polyether polyols for rigid foams. Various polyether polyols with TDA as initiator were successfully synthesized and various formulations of polyurethane systems for rigid foams which satisfied the international standards for self-extinguishment were developed. A member of SODASO staff (Hajrija Sehovic) defended her masters thesis in this research and one professional paper was published.

The School of Polyurethanes (workshop) in Tuzla is a very significant result of implementation of the project DP/YUG/82/005. The School of Polyurethanes is held every year in September for a period of one week. The School of Polyurethanes (I and II) started with lectures of experts from the Polymer Institute, attended by, along with the SODASO staff, members of industry and universities from all Yugoslavia. At the third (III) School of Polyurethanes, held in September 1985,

along with lectures given by two experts from the Polymer Institute, lectures were given by one expert from Great Britain, one expert from Yugoslavian industry, and one staff member of the SODASO Institute. At the fourth (IV) School of Polyurethanes to be held in September of this year (1986), along with experts from the Polymer Institute, lectures will be given by three experts from Great Britain, two experts from U.S., one expert from Poland, two experts from universities in Yugoslavia and , most importantly, four staff members from SODASO Institute.

Besides the lectures, thematic discussions will be held at which questions concerning the problems of polyurethane production will be discussed, as at previous schools.

The lectures of the staff from the Polymer Institute, held in Tuzla, initiated the formation of the School of Polyurethanes on a permanent basis. At the fourth School, three staff members of the SODASO Institute who completed the training at the Polymer Institute in Detroit will be lecturing.

The School of Polyurethanes offers the opportunity for the members of the Yugoslav industry to be informed every year of up-to-date achievements in the field of polyurethanes worldwide. Also, the School offers the opportunity to discuss directly with experts from developed countries of problems in the production of polyurethanes.

#### IV. RECOMMENDATIONS FOR FUTURE PROGRAMS

The previous trainees from Yugoslavia have all been excellent students and workers. It would be highly desirable for future trainees to be of the same or similar caliber as the previous trainees.

It is recommended that areas for future projects include sealants, elastomers, coatings, RIM, and high temperature resistant urethane based polymers. These are important areas since Yugoslavia is a large producer of isocyanates and new and additional outlets for the products of Yugoslav industries must be developed.

It is proposed to also continue training in the previously discussed important areas in polyurethanes.

In conjunction with the above, staff from Polymer Technologies, Inc. will participate in a polyurethane workshop (UNIDO sponsored) held at the School of Urethanes in Yugoslavia.

In the future, in addition to the previously described training programs, offers for research fellowships and post-doctoral appointments to Yugoslav personnel will be made.

#### V. BUDGET

Several notes must be made in connection with the budget.

1. Instead of 11 trainees, 13 people have visited the Polymer Institute and 2 more are scheduled to arrive in November, 1986. The total cost for these two (3 months each) is \$4,500.00. This will complete the entire \$100,000 budget.



2. The time span of the original contract was extended beyond our control, at the request of Yugoslavia.

3. The two additional trainees, who will spend 3 months each, will be trained on actual industrial projects going on in the Institute.

TABLE I

## Program for Cooperation with the Polymer Institute

SPECIFIC TIME PERIOD	SUBJECT	TIME DURATION	PERSONS
11/01/84 - 01/31/85	Polyurethane Coatings	6 months	Mediha Ahmetovic
04/01/86 - 06/30/86			
11/01/84 - 01/31/85	Polyurethane Adhesives and Sealants	3 months	Marija Vranes
02/01/85 - 04/30/85	Rigid Polyurethane Foams	3 months	Irfan Buxuladzic
04/01/85 - 06/30/85	Flexible Polyurethane Foams	3 months	Radojka Dobrosavljevic
04/01/86 - 07/15/86	Polyurethane Elastomers	3½ months	Mevlida Vlajic
04/01/85 - 09/15/86	Polyurethane Microcellular Elastomers	6 months	Bozo Banjanin
11/01/84 - 01/05/85	Structure-Property Relationships of Polyurethane Elastomers	2 months	Ivan Javni
01/01/85 - 04/30/85	Marketing Studies of Polyurethanes	4 months	Dragan Erkic
01/01/85 - 03/31/85	Marketing Studies of Polyurethanes	3 months	Jusuf Suljkanovic
01/01/85 - 06/30/85	Marketing Studies of Polyurethanes	6 months	Jasminko Arnautovic
04/01/86 - 7/08/86	Flammability Studies of Polyurethane and Polyisocyanurate Foams	3 months	Hajrija Sehovic
02/15/86 - 08/13/86	Research of Polyisocyanate - Based Polymers and Copolymers	6 months	Aisa Sendijarevic
03/15/86 - 08/13/86	Research and Development of New Types of Polyethers	6 months	Vahid Sendijarevic

TABLE II  
Equipment

Oxygen Index	Steam Heated Rubber Mill
Rohm and Haas Smoke Density Chamber	Water Detector-Analyzer
Liquid Chromatograph	Rheovibron (Dynamic Mechanical Spectrometer)
Differential Scanning Calorimeter	Gas Chromatograph
Thermal Conductivity Instrument	Gas Transmission Tester
High Performance Liquid Chromatograph	Butler Chimney
Thermogravimetric Analyzer/ Differential Thermal Analyzer	Weather-o-Meter
Infrared Spectrophotometer	Plastic Impact Tester-fully instrumental
Instron Universal Tester	Capacitance Measuring Assembly
Gel Permeation Chromatograph	Fourier Transmission Infrared Spectrometer
Radiation Detector-Analyzer	Thermomechanical Analyzer
Oscillating Disk Rheometer	Electron Spin Resonance
Torque Rheometer-Haake	Nuclear Magnetic Resonance
Variable Speed Rubber Mill	Thickness Gauges
High Pressure Stirred Reactor	
Electro-static Powder Coating	
Electro-deposition	
Dry Box	
Torque Rheometer-Brabender	
Injection Molder-Laboratory	
Extruder-Laboratory	
Paint Grinder	

INVITEE'S ANALYSIS OF COST PROPOSAL

**PART I**

**1. PROFESSIONAL SERVICES**

**A. Project Area**

<u>Position Title</u>	<u>Man Months</u>	<u>Cost per Man Month</u>
.....	.....	.....
.....	.....	.....
.....	.....	.....
.....	.....	.....

**TOTAL PROJECT AREA**

**B. Home Office University of Detroit,  
Detroit, Michigan (USA)**

<u>Position Title</u>	<u>Man Months</u>	<u>Cost per Man Month</u>
02 Instructional Staff	See Attached Explanation	.....
02 Univ. Researchers	.....	.....

**TOTAL HOME OFFICE**

**2. SUBSISTENCE**

**A. Project Area**

...35 man/days at \$....70.... per day.

**B. Briefing and De-briefing**

...6 man/days at \$....60.... per day.

**C. Other (specify)**

...60 man/days at \$....50.... per day.

**TOTAL SUBSISTENCE**

**3. TRAVEL AND TRANSPORTATION (specify in PART II B below)**

**4. REPORTS**

**5. OTHER DIRECT COSTS (specify)**

- ..... Indirect Costs (Accounting) .....
- ..... Clerical Support at Home Office .....
- ..... .....

**TOTAL OTHER DIRECT COSTS**

**TOTAL COST**

.....	\$.....
.....	\$.....
.....	\$.....
.....	\$.....
<b>TOTAL PROJECT AREA</b>	\$.....
<b>TOTAL HOME OFFICE</b>	\$.....
<b>TOTAL PROFESSIONAL SERVICES</b>	\$.....
<b>2. SUBSISTENCE</b>	\$.....
<b>3. TRAVEL AND TRANSPORTATION</b>	\$.....
<b>4. REPORTS</b>	\$.....
<b>5. OTHER DIRECT COSTS</b>	\$.....
<b>TOTAL OTHER DIRECT COSTS</b>	\$.....
<b>TOTAL COST</b>	\$.....

(continued)

6. EQUIPMENT, MATERIALS AND SUPPLIES

Equipment

Materials and Supplies

TOTAL EQUIPMENT, MATERIALS AND SUPPLIES

7. SUBCONTRACTS (specify)

.....  
.....

TOTAL SUBCONTRACTS

8. GRAND TOTAL ITEMS 1 - 7 CONTRACT PRICE:

TOTAL COST

\$.....13,075.\*.....  
\$.....7,400.....  
\$ 14,075

\$.....  
\$.....  
\$.....  
\$.....

PART II

Total Direct \$ 96,325.00

A. CURRENCY REQUIREMENTS

- a) Contractor's Currency \$.....97,136.....
- b) Local Currency \$.....2,450.....
- c) Other Currency \$.....414.....

Indirect

3,675.00

Total Contract

\$ 100,000.00

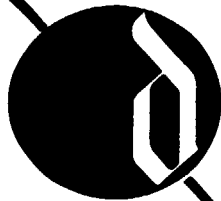
B. TRAVEL AND TRANSPORTATION EXPENSES (List - See Instructions, para. 3)

Travel and Transportation costs of \$5,500 have been budgeted to cover the travel of the Yugoslav researchers travel to various sites of research and production within the United States. All travel to be determined at a later time, will be coach class.

\$5,500

Travel by Instructional Staff to Yugoslavia is expected during project period, and will be charged at coach class at the prevailing rate. The estimated cumulative costs for travel by Instructional Staff.

\$4,136



# POLYMER TECHNOLOGIES INC.

## NEWSLETTER

A SUBSIDIARY OF THE UNIVERSITY OF DETROIT

AUTUMN 1986

## New venture builds on 18 years of polymer research at University of Detroit

Polymer Technologies, Inc. (PTI), the first corporate subsidiary of the University of Detroit, was formed in May 1986 and is an outgrowth of the University's Polymer Institute, established by Dr. Kurt C. Frisch in 1968. The new venture, PTI, will strengthen the established research effort in all areas of polymer chemistry and technology with the addition of administrative, financial and marketing services. An effective blend of business acumen and polymer research, PTI continues to be sensitive and responsive to the needs of private industry and public agencies.

PTI will remain a cost-effective source of research and development work for both large and small organizations. The professional staff can either complement the in-house R&D effort of a large company or act as the sole

R&D facility for a smaller firm.

The president and chief executive officer of PTI is Nicholas J. DeGrazia, Ph.D. Dr. DeGrazia will continue as the university's vice president for finance and treasurer, a position he has held since 1981. He comes to PTI with extensive background in business management and is credited with introducing innovative programs and techniques that have strengthened the university's financial position.

Kurt C. Frisch, Ph.D., will serve as PTI's vice president and director of research. As a researcher and educator, Dr. Frisch is recognized throughout the world for his considerable contribution to the field of polymers, particularly polyurethanes.

### This issue

#### ■ Who we are

The research staff  
Pages 2-3

#### ■ Clients

Past, present  
Page 4

#### ■ Board of Directors

Pages 2-3

#### ■ POLYMER TECHNOLOGIES, INC.

4001 W. McNichols  
Detroit, Mich.  
48221 USA

313-927-1565

#### President

Nicholas J.  
DeGrazia, Ph.D.

#### Vice president

Dr. Kurt C.  
Frisch, Ph.D.

## What we do: An overview of basic and applied research capabilities

PTI's research team can provide characterization, evaluation and synthesis of polymeric materials as well as new product development and market analysis. Major areas of research include:

- Catalysis and kinetics of polymerization reactions
- Structure-property relationships of polymer materials
- Modification of polymer materials
- Interpenetrating Polymer Networks (IPNs), polymer blends and polymer alloys
- Coatings
- Elastomers
- Foams
- Adhesives
- Sealants
- Flammability studies
- Degradation and stabilization of polymers
- Monomer and polymer synthesis
- Morphology
- Rheology
- High temperature polymers
- Reinforcement of plastics

Recent studies include the following:

- Improved catalysis performances or competing isocyanate reactions through high performance liquid chromatography
- Synthesis of unique two and three component IPNs
- Flame and smoke suppression of polyurethane foams
- Polyurethane composites as replacements for plaster of Paris
- Rigid, high-density, urethane-modified isocyanate foams as wood substitutes
- RIM and RRIM systems
- Hot melt polyurethane elastomers and adhesives
- IPN coating for automotive industry
- Urea/Formaldehyde foams
- Polyurethane ionomers (synthesis, structure, properties)
- Ionomer IPN coatings
- Ionomer pu foams
- Energy absorbing polymeric systems
- Thermally stable engineering plastics

**Reverend Robert A. Mitchell, S.J.**  
**President**  
**University of Detroit**  
**Chairman of the Board**  
**Polymer Technologies, Inc.**

**Louis Betanzos**  
**Executive Vice President**  
**National Bank of Detroit**

## Dr. Kurt C. Frisch

### Position:

Vice President and Director of Research, PTI; Professor of Polymer Engineering and Chemistry, University of Detroit.

### Education:

Undergraduate and graduate training at Universities of Vienna and Brussels. M.A. and Ph.D. degrees, Organic Chemistry, Columbia University.

### Past Work:

Research Chemist, General Electric Co.; Manager of Research, E.F. Houghton Co.; Director of Polymer Research and Development, Wyandotte Chemicals Corporation; Director of Research, Polymer Institute, University of Detroit. Co-Author and/or editor of 24 books, over 170 articles, 50 U.S. patents and hundreds of foreign patents.

### Research Interests:

All areas of polyurethane chemistry and technology, interpenetrating polymer networks (IPNs) and other polymer alloys, flammability of polymers, medical application of polymers, and structure-property relationships.

### Honors:

Considered a pioneer in polyurethanes, Dr. Frisch has received a number of awards, including:

#### 1986

Award for Outstanding Achievement in Plastics Education, Society of Plastics Engineers, Boston, Massachusetts.

(cont'd. pg. 4)

## Dr. Kaneyoshi Ashida

### Position:

Associate Research Scientist and Laboratory Director, PTI; Research Professor, University of Detroit.

### Education:

B.S., Chemistry, Tokyo Institute of Technology; D. Eng., Tokyo Institute of Technology.

### Past Work:

Research Chemist, Naval Chemistry Laboratories; Supervisor, Central Research Laboratories, Hodgegaya Chemical Ind. Ltd.; Director, Chemical Research Laboratories, Nisshinbo Industries Co., Ltd.; Director, Urethanes Research Department, Mitsubishi Chemical Ind., Ltd.; Executive Technical Counselor, Mitsubishi Chemical Ind., Ltd. Author of 52 papers, 14 books and holder of over 100 patents.

### Research Interests:

Synthesis and application of plastic foams, including polyurethane foams, polyisocyanurate foams, polyoxazolidone foams, flame retardant foams. Nylon 6 IPNs, liquid crystal polymers, exploratory studies in novel catalysts in isocyanate reactions, synthesis and characterization of high-temperature resistant polymers.

### Honors:

#### 1985

FSK Medal of Merit, awarded by the German Foam Society for his pioneering work in the introduction of polyisocyanurate foams into the Japanese and U.S. foam industries, and his many contributions to the field of polyurethane, polyoxazolidone and other isocyanate-based foams.

## Dr. Daniel Klempner

### Position:

Associate Director of Research, PTI; Research Professor of Polymer Chemistry, University of Detroit.

### Education:

B.S., Chemistry, Rensselaer Polytechnic Institute; M.A., Chemistry, Williams College; Ph.D., Physical Chemistry, State University of New York, Albany, New York.

### Past Work

Polymer Engineer, Sprague Electric Co.; Visiting Scientist, Polymer Science & Engineering Program, University of Massachusetts; Research Professor, Polymer Institute, University of Detroit. Author of over 90 articles, 6 books and holder of numerous patents.

### Research Interests:

IPNs, polymer alloys, polyurethanes of all types, energy absorption in polymeric systems, high-temperature polymers, coatings, elastomers, foams, flammability of polymers, structure-property relationships, catalysis of polymerization, medical applications of polymers.

### Honors

#### 1982

Baekeland Award Nominee

#### 1984

Best Paper: Society of Plastics Industry meeting, Polyurethane Division Conference

## Board of Directors

● ●  
**Robert G. Decraene**  
 Regional Managing Partner, Midwest  
 Coopers & Lybrand

● ●  
**Kenneth F. Elliott**  
 President  
 Kenmar Corp.

● ●  
**Oscar A. Lundin**  
 retired Vice Chairman  
 General Motors Corp.

● ●  
**Dr. Jiri E.  
 Kresta**

**Position:**

● ●  
 Senior Research Scientist, PTI;  
 Research Professor of Polymer  
 Science, University of Detroit.

**Education:**

● ●  
 M. Chem. Eng. and M.S., Nuclear  
 Chemistry, Institute of Chemical  
 Technology (Prague, Czechoslo-  
 vakia); Ph.D., Polymer Science  
 Macro-molecular Institute, Czech-  
 oslovak Academy of Science  
 (Prague).

**Past Work:**

● ●  
 Research Scientist, Research Insti-  
 tute of Synthetic Rubber, Gott-  
 waldov, Czechoslovakia; Research  
 Scientist, Institute of Macromol-  
 ecular Chemistry, Brno, Czech-  
 oslovakia; Research Associate,  
 Wayne State University; Research  
 Professor, Polymer Institute, Uni-  
 versity of Detroit. Author of over 70  
 papers, 5 books and holder of  
 numerous U.S. and foreign patents.

**Research Interests:**

● ●  
 Polyurethanes, polymer degradation  
 and stabilizations, structure-property  
 relationships, high-temperature re-  
 sistant polymers, flammability, kinet-  
 ics and catalysis of polymerization  
 reactions, coatings and foams.

● ●  
 Recently conducted studies in engi-  
 neering alloys and alcohol-soluble  
 polyurethane elastomers.

● ●  
**Dr. Michael O.  
 Okoroafor**

**Position:**

● ●  
 Associate Scientist, PTI; Assistant  
 Professor, Organic and Polymer  
 Chemistry, University of Detroit.

**Education:**

● ●  
 B.S., Chemistry, University of Nige-  
 ria; M.S.E.C. (emphasis on Poly-  
 mers), University of Detroit; Ph.D.,  
 Synthetic Organic Chemistry, Mich-  
 igan State University.

**Past Work:**

● ●  
 Metallurgical Chemist, Nigerian  
 Steel Development Authority.

**Research Interests:**

● ●  
 Synthesis and characterization of  
 novel thermostable polymers, den-  
 tal applications of ring-opening poly-  
 merization, polymer supported cat-  
 alysts and NMR studies of polymer  
 structures.

● ●  
**Dr. Shaio-Wen  
 Wong**

**Position:**

● ●  
 Senior Research Scientist, PTI; Re-  
 search Professor, University of  
 Detroit.

**Education:**

● ●  
 B.S., Physical Chemistry, National  
 Taiwan University; M.S., Chemistry,  
 University of Oregon; Ph.D., Physi-  
 cal Chemistry, University of Michigan.

**Research Interests:**

● ●  
 Polyurethanes, structure-property  
 relationships, high-temperature  
 polymers, elastomers, medical appli-  
 cations of polymers, isocyanurate-  
 containing polymers, oxazolidone  
 chemistry and the effect of catalysts  
 on the isocyanate reactions by high  
 performance liquid chromatography.

● ●  
**Dr. Han X.  
 Xiao**

**Position:**

● ●  
 Research Scientist, PTI; Research  
 Professor, University of Detroit.

**Education:**

● ●  
 B.S. and M.S., Polymer Chemistry &  
 Engineering, Chandu Institute of  
 Technology; Ph.D., Polymer Chem-  
 istry, Chandu Institute of Organic  
 Chemistry Chinese Academy of  
 Sciences.

**Research Interests:**

● ●  
 IPNs with charge groups, structure-  
 property relationships, modifica-  
 tions of polymers, polyurethanes,  
 epoxies, acrylic polymers, elastom-  
 ers, coatings, adhesives, and seal-  
 ants from polyurethanes. Recently  
 developed new materials such as  
 coatings, foams, adhesives, based  
 on ionomer IPNs and blends.



## **New processing facilities add to capacity**

Current instrumentation includes state-of-the-art equipment for polymer characterization and determination of polymer properties with modern computer facilities. In November 1986, PTI will begin construction of a new processing laboratory of approximately 5,000 square feet. This new facility will include a lab RIM machine, a small foam machine, lab injection molder, a lab extruder, extrusion thermometers, rubber mill, Banbury mixer and environmental chamber. In addition, polymer characterization instrumentation will be housed in this location. This new facility will complement three material laboratories on the campus.

## **Clients: Past and present**

Polymer research and development services have been provided to over 120 companies. In addition, basic and applied research projects have been undertaken with the National Science Foundation, American Chemical Society and the departments of the Army, Navy and Air Force. Current corporate clients include automotive manufacturers, petrochemical companies, automotive suppliers, computer manufacturers, recreational equipment companies, medical suppliers and pharmaceutical firms. PTI is currently working with 20 clients.

## **Frisch (Cont.)**

### **1984**

Polyurethane Hall of Fame, San Antonio, Texas. Awarded by the Society of Plastics Industries. Dr. Frisch is only the second person to receive the honor and the first American. The other recipient was Otto Bayer, a German scientist.

### **1982**

Medal of Merit — of the British Rubber and Plastics Association, London, England. The first American to receive the honor in recognition of his pioneering research in the area of flexible and rigid foam, elastomers and coatings.

### **1981**

FSK, Medal of Merit, Dusseldorf, Germany. Awarded by the German Foam Society for his contribution to the development of urethane and isocyanurate foams.

### **1975**

IR-100 Award, Chicago, Illinois. The Industrial Research Award is given for the 100 top inventions of the year. Dr. Frisch received his for the development of hydrophilic urethane foams.