

COLLABORATIVE RESEARCH ON POLYMERIC MATERIALS THROUGH IUPAC

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Abstract - A very brief description of the history and development of the IUPAC organisation shows that the Macromolecular Division (IV) is unique in the way it provides a neutral international forum through which Working Parties of industrial and academic polymer scientists arrange collaborative research programmes and publish their results. In particular, the growth of Working Party IV-2-1 dealing with the "Structure and Properties of Commercial Polymers" is considered and, inter alia, answers are provided to questions such as "who's in it and how did they get in?", "what do they get out of it?," "how can competitors engage in collaborative research?," "is it really international?" and "who pays?". Mention is also made of the Working Party's contribution to the literature in recent years, of its perceived value and of the work currently in hand.

INTRODUCTION

Whilst it is easy to begin at the beginning, which I shall do, it is impossible for this particular topic to go on till I get to the end and then stop. The end is still unfolding, quite rapidly, and the best I can do is to provide a picture of the current position.

Following a very brief, but necessary, outline of the Union itself, I will concentrate on the way in which the Macromolecular Division, its Commission on "Polymer Characterisation and Properties" and in particular its Working Party on "Structure and Properties of Commercial Polymers" has found it possible to encourage collaborative work between industrialists, academics and scientists from other institutions at a very limited cost to the Union.

The success of this approach is gauged not only by any published contribution to the literature, but also, of course, by the value of the collaborative association to the individuals involved and by the influence this has on their own work or that of their colleagues or students.

THE INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

In the beginning, however, IUPAC was formed in 1919 as a voluntary, non-Governmental, non-profit association of organisations, each of which represents the chemists of a member country.

Its objectives continue to be:

to promote continuing co-operation among the chemists of member countries,

to study topics of international importance to pure and applied chemistry which need regulation, standardisation or codification,

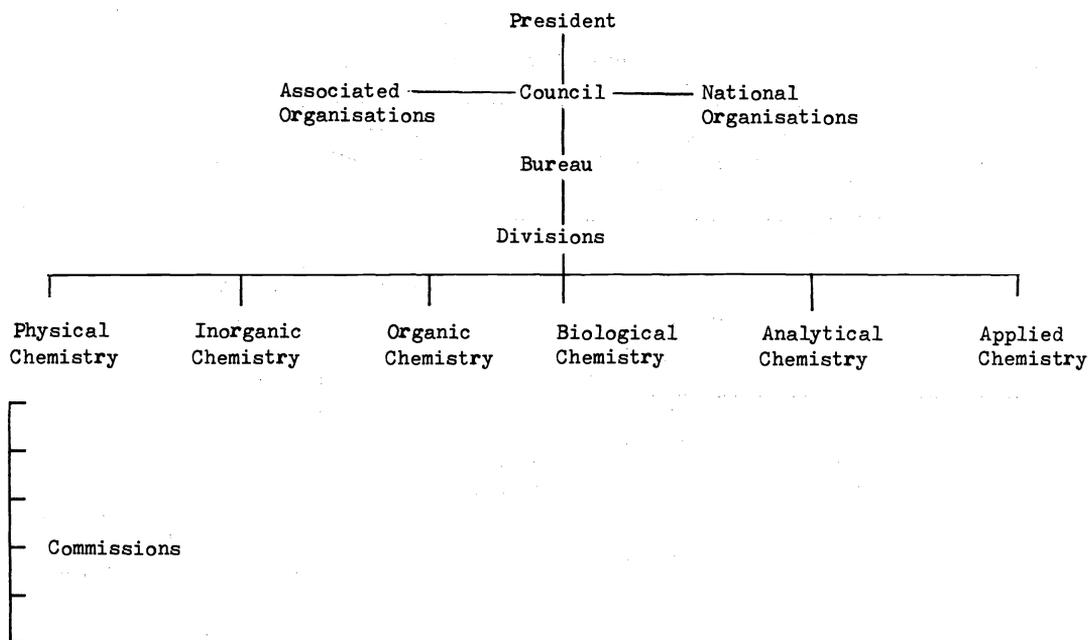
to co-operate with other international organisations which deal with topics of a chemical nature,

to contribute to the advancement of pure and applied chemistry in all its aspects.

Initially, of course, there were relatively few members and progress was quite slow. There was, however, a rapid expansion of activities following World War II and the need to divisionalize became evident; thus it was in 1949 that six Divisions were formed (see Figure 1), of these the five major, fundamental Divisions of Physical, Inorganic, Organic, Analytical and Applied Chemistry still exist.

Figure 1

FUNDAMENTAL ORGANISATION OF IUPAC



Each Division is divided into a number of Commissions, each one responsible for an area of chemical science. For example, the Physical Chemistry Division currently operates six Commissions with interests ranging from "Physicochemical Symbols, Terminology and Units" through "Electrochemistry" to "Molecular Structure and Spectroscopy".

Typically a Commission will have eight Titular Members, whose limited expenses for attending Commission meetings are funded by IUPAC, about an equal number of Associate Members and some National Representatives. Members are chosen, of course, both for their international expertise, as well as to complement each other.

It became apparent quite soon that the six classical Divisions of the Union did not truly correspond to the actual interdisciplinary character of modern science, especially chemistry. In the early sixties, for example, there was a Polymer and Plastics Section of the Applied Chemistry Division and a Macromolecular Commission of the Physical Chemistry Division. Both groups recognised the impossibility of separating chemistry and physics in the study of macromolecules when the new Macromolecular Division was established in 1967. At this time, too, the Biological Chemistry Division was dissolved.

Over the same period it became increasingly obvious that better ways would have to be found to encourage industrial support for, and involvement in, the Union which originally, through the National Organisations, had been almost entirely academic in membership. To this end a Company Associateship scheme was inaugurated in 1966; more recently Companies have been able to exert a direct influence on IUPAC affairs through the Committee for Chemistry and Industry set up in 1977; this is now one of six special Committees reporting to the Executive Committee.

There are now seven Divisions operating, the original five fundamental ones plus the Macromolecular Division and the Clinical Chemistry Division, involving the membership of 44 countries, some 140 Associated Companies, 1,000 or more individual scientists and an annual budget of around \$0.5 million. The broad picture is as indicated in Figures 2 and 3.

THE MACROMOLECULAR DIVISION

The foundation of the Macromolecular Division was laid in 1965 when work began on a programme to characterise two commercial grades of polystyrene and to compare their performance properties; this involved some 15 scientists from 8 industrial laboratories and several academic and Government laboratories. Each member of the group contributed actively to progress, the work was successful and led to an IUPAC publication and the

Figure 2

CURRENT ORGANISATION OF IUPAC

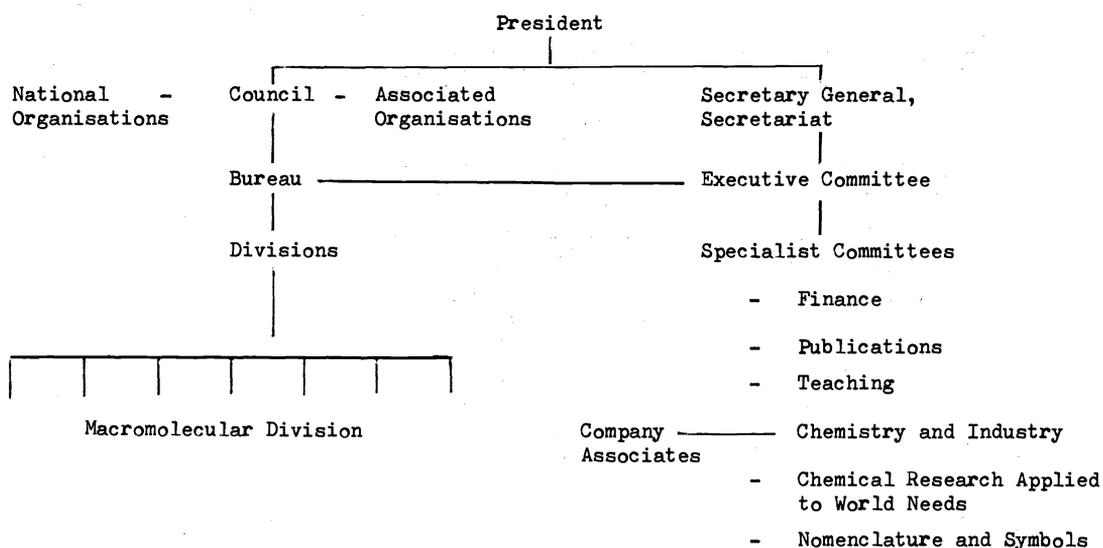


Figure 3

APPROXIMATE BREAKDOWN OF INCOME AND EXPENDITURE

Income		Expenditure	
Organisations	62%	Commission Meetings and General Assembly	54%
Company Associates	17%	Office expenses	36%
Interest/other	21%	Other	10%

"Working Party" approach became a template for future activities. Commercial grades of polymer were deliberately chosen for this programme to encourage industrial involvement as well as to satisfy the potential need for large quantities (tonnes) of consistent product.

The procedure for project selection is as follows:-

1. Division or Commission Committee establish where there is a clear need for more scientific information.
2. A draft project outline is proposed.
3. A decision is taken on whether the project can best be handled by an existing group or whether a new Working Party is needed.
4. A project leader is selected; the ongoing work is collated by one or more members of the group who also prepare the final report.

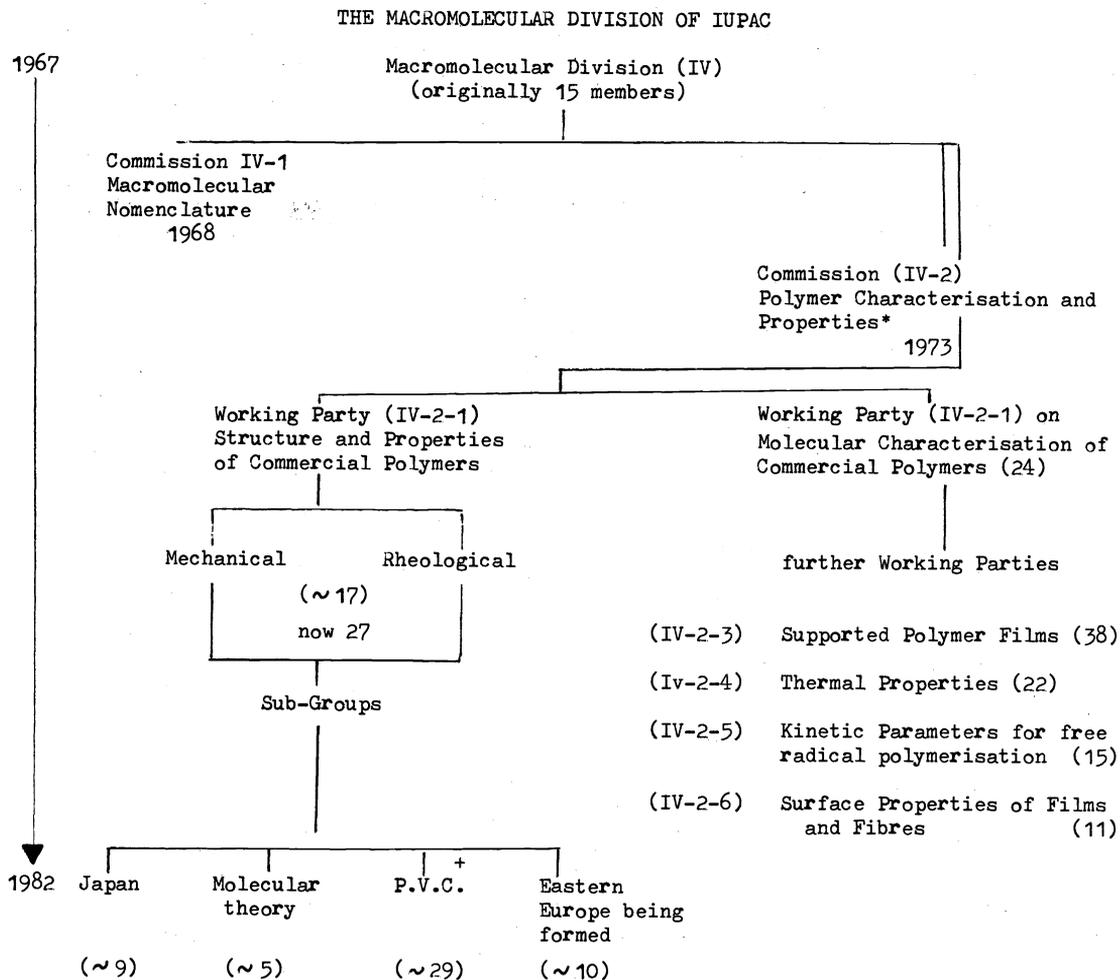
Over the years the adoption of this procedure has led to the Division growing from about 15 participants to the 200 or more today as shown in Figure 4.

What then is the secret of the Working Party approach that has made it so successful? This lies in their various Rules which, whilst not totally uniform across the board, always include:

1. Every member of a Working Party or project must contribute to the work programme.
2. All results of collaborative programmes must be published, preferably in Pure and

Applied Chemistry, the official journal of IUPAC.

Figure 4



* The Chairmen of the Working Parties are the Titular Members.

+ "Characterisation and Estimation of Defects in the Molecular Structure of PVC"

3. Working Parties and Project Groups are expected to be self financing although small funds are available to meet some costs of collaborators in exceptional cases.
4. Membership is freely open to any organisation provided it is represented by a polymer scientist of repute.

In the case of Working Party IV-2-1 on the "Structure and Properties of Commercial Polymers" there is also, I believe, an important informal understanding. No member has any inhibitions at all about asking raw material suppliers for more detailed information on a polymer nor does he feel disenchanted if the reply is, in essence, "I have it but I will not give it to you". Finally, there is a Rule that members must attend at least one meeting a year. These are normally held by invitation and rotation at the various sites of the industrial members; this not only saves money but also allows, after the normal 1.5 days of meeting, a tour round those laboratory facilities of the host that he wishes to show.

There is also a further Rule that states that all participants in a programme receive copies of all working documents; all members of the Working Party receive copies of progress or draft reports written by programme co-ordinators.

This particular Working Party currently has 34 active participants, nearly two thirds of whom work in industry, belonging to 27 organisations from 9 countries. The Working Party

was almost entirely European when it began, but support has recently been growing elsewhere, particularly in the U.S.A.; in fact, the first Working Party meeting to be arranged outside Europe took place in the United States last year.

Travelling to distant meetings is obviously expensive, however, and in order to provide a framework for collaboration at minimal cost, the Working Party is in the process of setting up Regional Sub-groups; for example, one was started recently in Japan and in Eastern Europe progress is being made towards starting another.

THE MEMBERSHIP AND PROGRAMME SELECTION OF WORKING PARTY IV-2-1

The membership of the Working Party is broad, and growing. It is not so much individuals as organisations that formally apply for membership, although applications are considered by the Working Party in terms of who it is that is to represent the organisation and the scientific contribution that can be expected from them.

Organisations currently involved are given in Table 2; this list does not extend to the many more organisations involved in Sub-group membership.

Because the Working Party normally meets for two relatively separate meetings each year - each involving one of the two projects authorised by the Commission, namely rheology or mechanical properties - organisations are often represented by two "specialists" rather than by one broader polymer scientist.

At any one meeting of the Working Party there will be about 20 delegates and, typically, five or six programmes will be discussed. Work on these programmes will obviously be at different stages from initiation to the agreement of a final report for publication; the time-scale of a programme normally extends from 3 - 5 years although both shorter and longer ones are known.

Although all members have to work on at least one programme they do not have to work on all, although many work on two or three. There will thus be a number of often overlapping groups working on the different Working Party programmes, each of which is the responsibility of an agreed co-ordinator. This last is a time consuming, challenging task, although not, I hope, without reward.

As part of its agenda at each meeting the Working Party considers what new programmes it might undertake. Anyone is free to make suggestions and they do. Only if some 6 or more members express an interest in contributing and indicate what experimental (or theoretical) facilities they propose to deploy is the proposer, who also, of course, usually turns out to be the co-ordinator, asked to produce a formal written proposal setting down the objectives, the suggested experimental scheme and the availability of raw materials. Such a proposal is prepared in between annual meetings and whilst much is agreed by correspondence between the expected collaborators, there is usually some considerable refinement of the programme during a finalising discussion at the next meeting. There is an annual presentation for each current programme, depending upon its status, of a progress report, a draft final report or final report.

Virtually all of the Working Party's reports have been published in Pure and Applied Chemistry, although on occasions near similar papers have also been published in Journals more avowedly "polymeric". Opportunity is also taken, of course, to present papers to any appropriate IUPAC meeting; indeed two Working Party papers have already been presented here.

PROGRAMMES OF WORKING PARTY IV-2-1 PAST AND PRESENT

The essential philosophy behind the programmes is to elucidate the structure-property relationships of commercial polymers through carrying out a wide range of property measurements, including processing measurements, on samples whose molecular characteristics are as completely determined as is possible. By deploying a few of the facilities of each of many laboratories it has been found that a significantly wider range of apparatus becomes available to the programme co-ordinator than any one laboratory can muster. Pooled resources can thus probe considerably further than can solo efforts; this has proved to be one of the main strengths of the Working Party system.

On occasions, however, programmes involving more immediately practically important phenomena are allowed to proceed with less rigorous structural characterisation.

Table 3 lists the titles of programmes that have been published in the last 7 years, and as can be seen one of these is itself a three part series, each of which is a major work in its own right.

Table 2

MEMBER ORGANISATIONS OF WORKING PARTY IV-2-1*

Industrial	Academic
BASF	Case Institute of Technology
Borg Warner	CNRS, Vernaison
B.P. Chemicals	Cranfield Institute of Technology
C de F Chimie	ETH, Zurich
Du Pont	IKT, Stuttgart
Hoechst	Institut Chemii Przemyslowej, Warsaw
Huls	M.I.T.
I.C.I.	University of Illinois
Monsanto	University of Massachusetts
Montepolimeri	University of Tennessee
Shell	University of Wisconsin
Solvay	University of Washington
Rheometrics	TNO, Delft
Rhone Poulenc	

* excluding the affiliations of Sub-Group members.

Table 3

PUBLICATIONS OF WORKING PARTY IV-2-1 FROM 1975

Basic parameters, melt rheology and end-use properties of three similar low density polyethylene samples. (1)
A collaborative study of capillary flow of highly lubricated unplasticised poly(vinyl chloride). (2)
A collaborative study on tensile properties of rigid PVC, long-time transition. (3)
The effect of molecular orientation on the mechanical properties of rubber modified polystyrene. (4)
Mechanical properties of rigid polyvinyl chloride - effect of fillers. (5)
A collaborative study of the melt rheology of a styrene-butadiene-styrene block copolymer. (6)
Sub-primary particles in PVC - Identification and elucidation of their role during flow. (7)
A study of impact strength testing and its relevance to real mouldings. (8)
The structure and properties of uni- and biaxially oriented polypropylene films. Part I - Structural characterisation; Part II - Mechanical and other end use properties. (9)
Constitutive equations from Gaussian Molecular Network Theories in Polymer Rheology. (10)
The relation between rheological properties and film blowing of two LDPE and two HDPE samples. (11)

It is not appropriate here to go into any real detail of these programmes but in the Appendix four Abstracts are quoted fully to indicate the breadth, depth and type of work involved. Hopefully some readers will have their appetites sufficiently whetted to turn to the originals in Pure and Applied Chemistry^{1,3-11} (with but one early exception² that helped make and prove the Rule about publication).

Programmes currently being pursued or developed include the following:-

- The stability of elongational flows of molten polyester and polyethylene.
- Extrusion instabilities of polyethylene including their role in processing operations.
- The rheology of the polyethylene film process.
- Fundamental problems in coextrusion.
- The rheology of polymer/particulate systems.
- Further investigation of impact testing.
- Finalising the draft of Part III of the programme on oriented polypropylene films.
- Fracture toughness - its assessment and meaning.

Furthermore there are a considerable number of possible programmes short-listed which will either be taken up in the future or superseded by some new projects of greater significance.

THE VALUE OF MACROMOLECULAR DIVISION WORK

Firstly, consider the value to the member and, through him, to his organisation. There are, I suggest, the following significant advantages:

- (i) the stimulating challenge of working with other experts to resolve a common problem
- (ii) the ability to tackle together work which one would like to do oneself but for which there are nowhere near enough resources of time and effort and often limitations of equipment.
- (iii) the availability of unusually well documented samples of polymer
- (iv) the fostering of academic/industrial relationships
- (v) the privilege of being invited to look around industrial and institutional laboratories
- (vi) the broadening of ones experience through close association with all the work going on, even on programmes in which there is no direct involvement

Secondly, consider the value of the work to the scientific community at large. Whilst really hard facts are difficult to come by it is fortunate, at least, that IUPAC has itself carried out a survey of the views of industrial chemists recently¹². Some paragraphs of this report are quoted below and the results of the survey are shown in Figure 5.

¹²Research directors of various chemical companies (IUPAC Company Associates in Czechoslovakia, Federal Republic of Germany, Israel, Italy, Sweden, Switzerland and USA) were asked to evaluate each publication published during the period 1974 - 1980, and provide a positive, negative or indifferent response. A rating of "no judgement" was applied when the participants were not familiar with the subject and unable to evaluate a report.

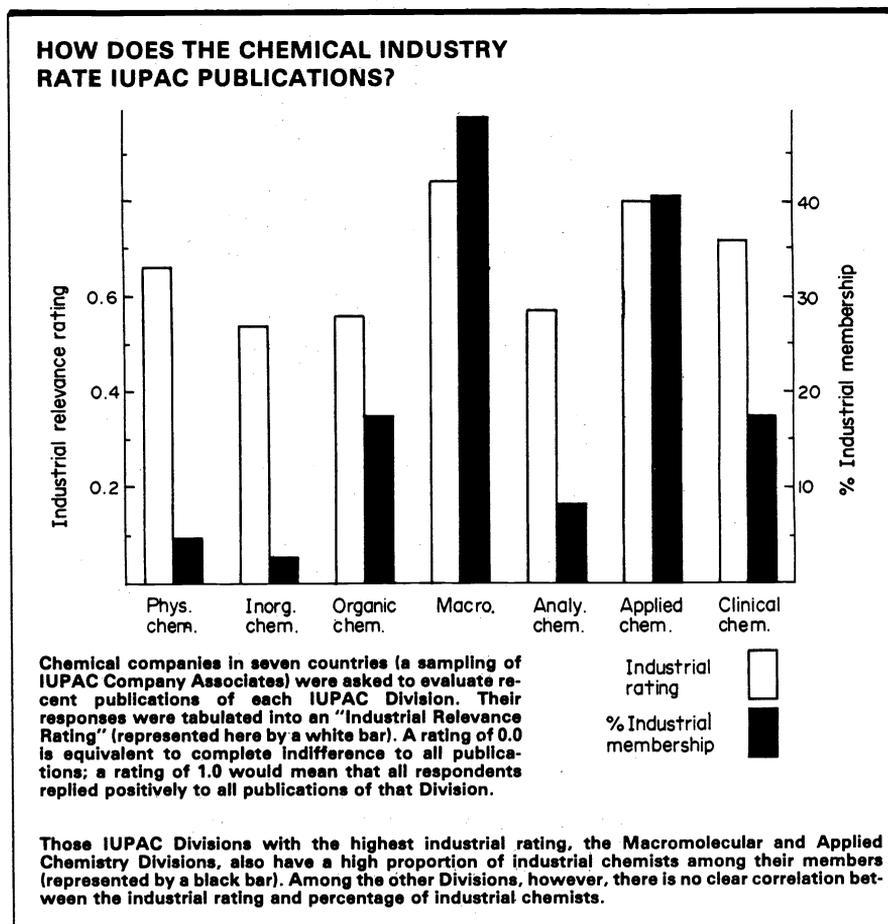
The survey results and comments of the participants, reveal a number of options that might allow IUPAC to become more responsive to the needs of the chemical industry. However, the limited scope of the survey must be borne in mind when the results are interpreted. For one thing, the survey reflects the views of industrial chemists only: academic chemists might have a very different outlook. Furthermore, respondents conceded that their judgements were often based solely on the title of the reports or a superficial reading. Survey participants usually gave positive or indifferent responses: very few reports were rated negatively. Thus, the survey results seem to reflect the relevance of IUPAC reports to industrial chemistry, rather than a rigorous evaluation of their quality.

In order to condense survey responses into a single meaningful index, Chemistry International compiled an "Industrial Relevance Rating" for the publications of each IUPAC Division. This rating reflects the relative approval, disapproval or indifference of all respondents. It disregards "no judgement" votes. The rate was defined so that a value of 1.0 would mean that all participants responded favourably to all publications of the Division; a value of 0.0 is equivalent to indifference by all participants. The rating is defined as:

$$\text{Relevance Rating} = \frac{\text{no. positive responses} - \text{no. negative responses}}{\text{total positive, negative and indifferent responses}}$$

The highest Industrial Relevance Rating was earned by the Macromolecular Division. To many, this might come as no surprise. The Macromolecular Division was formed (in 1967) to

Figure 5
(Reprinted from Ref. 12)



integrate chemists from industry, universities, government laboratories and independent institutes in collaborative studies dealing with commercial polymers. It is the only IUPAC Division whose membership is composed very nearly of equal numbers of industrial and non-industrial chemists. It has two Commissions: one dealing with macromolecular nomenclature, and a second concerned with polymer characterisation and properties, which operates the unique Working Party system. Of this latter Commission, the Research Director of a major US chemical company wrote, "All of the subjects under this Commission (12 papers) are of interest to industry. This Commission gets top rating both on number (of reports) and subject (matter)." His views are reinforced by the Vice-president of Research & Development of another US chemical company. He wrote, "I believe the Macromolecular Division has done very well on the relevance of its activities to industrial interests. Also, participation by industrial members in the Macromolecular Division is significant. With respect to industrial participation, this Division could possibly be used as a model for some of the other Divisions."

THE FUTURE

It is always dangerous to extrapolate the future from one's knowledge of recent history and the present. Over the last two years at a time of unparalleled difficulty for the polymer industry at large and of academic retrenchment rather than expansion, it is remarkable that enthusiasm for IUPAC work has remained so high. Certainly, programmes are tending to take longer to complete but the work is being continued and, with very few resignations and many applications to join Working Party IV-2-1, it seems likely that too many members, rather than too few, will encourage further organisational development. After all, one of the greatest assets of the Working Party principle is that of comfortable size encouraging around-the-table active participation of all members. If difficult times can be weathered so relatively easily, there can be little doubt about the future.

Certainly, there are a large number of fundamental problems still to be resolved; with the likely diminution of industrial research it would seem that many of those which relate to industrial needs will come to be solved more and more by collaborative work as time passes. If anything, academics will also be encouraged more to associate themselves with such work.

IUPAC offers an attractive environment for this type of co-operation and the Macromolecular Division, in particular, is establishing local geographical groups to provide opportunities for polymer scientists to contribute without having to travel half the world to do so. International co-ordination will present a major problem and, again, considerable organisational work will be needed to ensure that experimental effort is not wasted.

In short, the future looks more exciting than the past. What more can one ask ?

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APPENDIX

The following summaries of four of the papers prepared by Working Party IV-2-1 give a more detailed idea of the way in which the wide range of topics listed in Table 3 have been experimentally investigated.

- (Ref. 1) Basic Parameters, Melt Rheology, Processing and End-use Properties of Three Similar Low Density Polyethylene Samples.

Participants from six laboratories have collaborated in a comprehensive study of three LDPE samples A,B,C (all of melt index 1.5) which are indistinguishable on the basis of measurements of melt index at 190°C, intrinsic viscosity, and GPC. The samples exhibit significant differences in processing (maximum drawdown speed in film blowing) and end-use properties (optical quality of blown film).

Rheological measurements have been made on the molten polymers at 150°C. The three samples show substantially the same linear viscoelastic behaviour (within limits of ± 10 per cent) in oscillatory shear, in stress growth at the start of constant shear rate flow, and in stress relaxation, and have identical flow curves (viscosity versus shear rate). The three samples show differences in non-linear viscoelastic behaviour. In shear, these differences (in end correction, extrudate swell and first normal stress difference) are associated primarily with the elastic part of the melt deformation and are more pronounced at the lower shear rates ($0.01-0.1s^{-1}$). The melt index values at 125°C are different for A,B and C. In elongation the stress strain diagrams for A,B,C show significant differences if the elongation rate is low enough ($0.01-0.1s^{-1}$) and the elongation strain is high enough. Flow birefringence has been measured in the transient region following the start of constant shear rate.

An important conclusion of this work is that, for the particular LDPE samples chosen, there are substantial differences in processing behaviour and end-use properties of blown film which are reflected in certain non-linear elastic properties of the melts but not in the results of characterisation tests as commonly performed. The samples lie in the same order A,B,C for (1) increasing values of the critical drawdown speed (limited by bubble rupture in film blowing) and (2) of the optical quality of blown film (decreasing haze); (3) decreasing elastic contributions to the behaviour in shear flow; and (4) decreasing tensile stress in elongational flow (at low rates and large strains).

- (Ref. 4) The Effect of Molecular Orientation on the Mechanical Properties of Rubber-Modified Polystyrene.

Unoriented and oriented specimens of two rubber-modified polystyrenes (designated HIPS I and II) were examined by 8 members of the IUPAC Working Party "Structure and Properties of Commercial Polymers".

The raw materials were characterised by several methods. It was found that the two materials, apart from their different glass transition temperatures T_g (unlike HIPS II, HIPS I contains no paraffin oil as a lubricant), differ mainly with regard to their effective rubber phase volume; although both materials were prepared with the same rubber content, the rubber particles of HIPS II contain more polystyrene and therefore have a larger volume.

The molecular orientation of the stretched specimens, distributed to all participants as well as of the specimens stretched individually by some participants was determined by several methods (birefringence, linear thermal expansion, frozen-in stress, shrinkage). Because of its higher T_g , HIPS I becomes more highly oriented when both materials are stretched at the same temperature.

The dependence of the matrix orientation of the materials, as well as of the corresponding deformation of the embedded rubber particles, on the stretching conditions was examined. Owing to the molecular relaxation mechanisms, the orientation of the matrix relaxes during the stretching process. If the specimens are stretched with constant crosshead speed at sufficiently high temperatures, the generation and relaxation of orientation obeys the superposition principle, and in addition the generation of orientation follows a linear relationship with strain. Furthermore, if the materials are stretched within a suitable temperature range above T_g , some of their properties can be explained very well with the aid of the theory of rubber elasticity. The deformation of the rubber particles depends on the draw ratio of the matrix and on the stretching conditions. Only at low temperatures and short stretching times do the rubber particles deform in conformity to the matrix. Otherwise their deformation falls short of the matrix deformation.

The influence of orientation on the mechanical properties of the materials was also investigated. Strength and extensibility, both measured parallel to the direction of orientation, are improved by orientation. The unusual increase in extensibility is due to a transition from deformation by craze formation to deformation by shear yielding. - HIPS I is somewhat stronger, especially if it is oriented, and in the oriented state is able to deform more easily by shear yielding. On the other hand HIPS II, which tends more to crazing, shows, if not oriented, an extensibility that is considerably higher than that of the unoriented HIPS I. The mechanical properties of the oriented materials are definite functions of the molecular orientation of the matrix material, independent of the stretching conditions and of the deformation of the rubber particles.

(Ref. 8) A Study of Impact Strength Testing and its Relevance to Real Mouldings

The impact resistance of simple mouldings as assessed by various impact machines has been compared with that of standard specimens cut from them, as part of a search for test procedures that will give good correlations with the resistance of commercial end-products in service.

The falling dart tests appear to be the most versatile of those used in this programme and are particularly informative when the test conditions are such that the material under investigation is in, or near to, its tough-brittle transition.

(Ref. 11) The Relation Between Rheological Properties and Film Blowing of Two LD-PE and Two HD-PE Samples.

Two pairs of polyethylenes (HDPE, LDPE) were studied extensively in laboratory tests and in film blowing. Within each pair, the samples exhibit only small differences in the shear viscosity function, but large differences in film blowing, in crystallisation behaviour and in some rheological properties. The two HDPE samples were prepared from the same powder lot and differ by the kind of processing aid (zinc or calcium stearate) which was added before granulating.

The most sensitive laboratory tests involve extensional flow (extensional viscosity of steady uniaxial extension, tensile test, entrance flow into capillaries). Other sensitive laboratory tests are in shear when dominated by long time constants (zero viscosity, stress relaxation).

For both pairs, the sample with the lower extensional viscosity can be extended the most in the tensile test and can be blown into the thinnest film. Crystallisation and extensional rheology seem to be the two most important areas of laboratory testing, when distinguishing between polyethylene film blowing materials.