

conference papers

Speciality polymers: Prospect – Retrospect

Geoffrey Allen

Unilever Research and Engineering Division

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This conference, marks the 25th anniversary of POLYMER, a journal which serves a science and an industry little more than 50 years old. In fact it has served over a period in which the polymer industries' fortunes have undergone great change. The first 25 years of polymer science saw dramatic development in the understanding of polymer materials, outstripped only by the ingenuity of the chemists to produce a wide variety of chemically different polymers. It was a boom industry sparked off by science-lead innovation in the 30's, pulled on by the demands of World War II in the 40's and then transformed into a petrochemicals industry in the 50's. Towards the end of this period POLYMER was launched. Industry and Academy vied for the discovery of new polymers or new effects and industry scaled up polymer production, not always mindful of the development of markets. In the mid 60's the cost of the entrance ticket to become a large scale producer, the growing awareness of the need to know more about the downstream application and finally the 1973 oil crisis all contributed to dramatic changes in attitudes towards the future of the industry. Difficult rationalizations were put into train which have led in the last five years to substantial structural change in the basic industry. Some producers have withdrawn from segments of the industry, in some cases from segments which they pioneered; others have shut down obsolescent capacity or improved the cost-effectiveness of their operations. Thus the journal POLYMER has covered a period of painful change for the industry which inevitably has had its effect on the direction which research has taken. The drive to invent new polymers gave way to process development, to understanding the properties and processing of well-established polymers and to the study of copolymers and polymer blends as a way of obtaining desirable combinations of properties from well established monomers and polymers. In retrospect the industry is coming through a severe recession, but in prospect its fortunes seem brighter than might have been expected. The theme chosen to mark this 25th anniversary 'Speciality Polymers' testifies to the optimism abroad. The romantic period petered out in the early 60's, and in the mid 60's and 70's industry focussed its attention on more efficient processes and the overall economies of supply and demand. However, in the last 5 years we have witnessed a return to the exploitation of the unique properties of individual polymers, to the development of polymer-based systems to meet specific needs or performance criteria. This has given new heart to research workers who are skilled in the synthesis of new polymers or new forms of old polymers and bodes well for the creative scientist. And, of course, it is good news too for the editor seeking to fill his journal with stimulating and imaginative papers!

SPECIALITY POLYMERS—RETROSPECT

Before 1930 the polymer industry grew slowly, utilizing natural rubber, cellulosic derivatives and thermoset resins as the basic materials. The step-change which followed the growing impact of development of polymer chemistry in the 30's greatly expanded the range of synthetic polymers available, viz:

poly(vinyl chloride)	—CH ₂ CHCl—
polystyrene	—CH ₂ CH(Ph)—
poly(methylmethacrylate)	—CH ₂ C(CH ₃)(COOCH ₃)—
polybutadiene	—CH ₂ CH=CHCH ₂ —
nylon	—CO(CH ₂) ₄ CONH(CH ₂) ₆ NH—
polyethylene	—CH ₂ CH ₂ —
poly(vinylacetate)	—CH ₂ CH(OCOCH ₃)—


and a range of copolymers.

These are still part of the core group of polymers which form the high tonnage part of the polymer industry.

It is worth remembering that some were introduced with the connotation of being speciality materials and the fortunes of these polymers were strongly influenced by the demand for them in World War II. Polythene's special promise as an insulator in the electrical industry, the use of poly(methylmethacrylate) for the cockpit hoods of fighter planes and the value of nylon for parachute cord bore directly on their manufacture as strategic materials during the war. Several firms entered the postwar era with good manufacturing facilities. There are still a few special grades of these materials that command a premium price including:

- (i) Low dielectric loss polyethylene for submarine cables.
- (ii) Ultra high molecular weight polyethylene for hip joints.
- (iii) High impact poly(methylmethacrylate) for optical applications.
- (iv) Purified natural rubber for contraceptives.

In the postwar period, further developments in polymer chemistry added:

- (i) poly(ethylene terephthalate) —CH₂CH₂·OCO——OCO—
- (ii) high density polyethylene —CH₂·CH₂—
- (iii) polypropylene —CH₂·CH(CH₃)—

to the aforementioned group which constitutes the core of the commodity polymer business.

In the postwar period however a small number of unique speciality polymers were introduced which has not so far succumbed to commodity status. Indeed they have

never been surpassed by deliberate attempts to develop materials to improve on their individual unique attributes. Foremost amongst this group are:

(i) Polytetrafluoroethylene ($-\text{CF}_2 \cdot \text{CH}_2-$), a chemically inert, solvent resistant high melting machinable polymer with an unusually low coefficient of sliding friction.

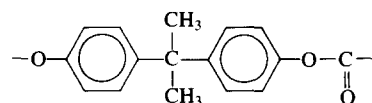
(ii) Poly(dimethylsiloxane) ($-\text{Si}(\text{CH}_3)_2\text{O}-$), at low molecular weight highly mobile oils, at high molecular weight a resilient rubber with the lowest T_g (-120°C) so far recorded.

(iii) Poly(vinylidene fluoride) ($-\text{CH}_2 \cdot \text{CF}_2-$), remains the polymer with the strongest piezoelectric effect.

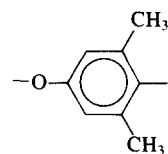
Polyacetal, an engineering polymer amenable to precision engineering and with a melting point excess of 160°C is another member of this group, but one which is under threat from more recent developments as I shall now record.

In the period '65 to '75 a second wave of speciality polymers appeared, all of which were characterized by a profile of good engineering properties such as toughness, stiffness, high tensile strength, abrasion resistance and temperature resistance up to *ca.* 200°C . The group includes:

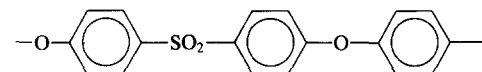
poly(bis-phenol 'A' carbonate)



poly(2,6-di-methylphenylene oxide)



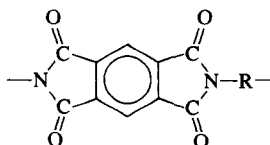
and several polysulphones, e.g.



Almost all the successful polymers in this group of 'engineering plastics' are paraphenylene-linked structures. Paraphenylene structures have been exploited, too, in a new generation of ultra high modular fibres from aromatic polyamides. Kevlar is one of the most highly developed materials of this type and is based on poly(*p*-benzamide)-type structures $-\text{CO}-\text{C}_6\text{H}_4-\text{NH}-$. As we

shall see one of the most important pointers to the future is that these materials are capable of self orientation in the melt and in solution to form liquid crystal structures which facilitate the drawing of the fibre.

Another distinct set of speciality polymers which were introduced in this second wave were the high temperature resistant materials which contain heterocyclic units in the main chain typified by the poly imides or benzimidazoles. A typical structure might be:



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Such polymers are not easy to synthesize because of their inherent insolubility. They are often physically intractable too and cannot be processed by melt-flow methods. Sintering is often the only route to forming, though fibres can be made too.

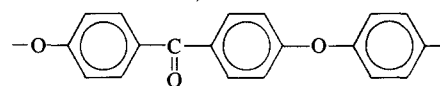
SPECIALITY POLYMERS—PRESENT

In the past decade the range of speciality polymers in the various categories mentioned in the previous section has gradually extended and there has been some weeding out.

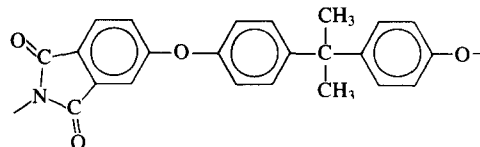
However, no serious competitors to PTFE, PDMS or PVF have appeared. Further, it is significant that all the speciality materials are essentially organic in nature. With the exception of some ceramic-type structures, PDMS remains almost the sole example of a successful inorganic polymer.

The group of engineering thermoplastics have been further extended with the development of:

poly ether ether ketone,



poly ether imide,



all seeking to edge-up the profiles of mechanical properties, temperature and/or solvent resistance at acceptable cost and processibility.

The work on high temperature resistant polymers typified by the polyimides has focussed mainly on more tractable synthetic results and solvent systems and has made slow progress.

But this decade has clearly established three other classes of speciality polymers:

- (i) adhesives
- (ii) photo resist polymers
- (iii) biomedical materials

The success of the fast curing high performance cyanoacrylates has led to the development of a host of adhesive systems made possible by precision polymer chemistry. Some of the adhesive films are essentially homopolymers, others are rubber reinforced plastic composites. Even polyimide-based adhesives are now available for use in the microelectronics industry to provide high temperature stability. Since some of these polyimide adhesive formulations contain 50–80% by weight of silver or gold powder, they must rate as the most expensive polymer systems offered for sale!

Photoresists are in great demand in the micro electronics industry and have a significant role in the improvement of resolution and precision in the etching of chips.

Biomaterials have to be either inert or bio compatible in their environment. The polymers, specially supplied, range from ultra high molecular weight polyethylene, polysiloxanes, and special urethanes to polymer structures devised to interact physically with biological tissue. Although there is a well defined market for special

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polymers, many of the structures are still custom-tailored to meet local requirements.

The upshot is that there is now an established speciality polymer market with considerable growth than now stands alongside the commodity polymer industry. Some idea of the range of speciality polymers available, and their prices is given in *Table 1*. This has to be read against a selling price of 35–40 cents/lb for commodity polymers such as polyethylene and polypropylene. Thus the prices for speciality materials are from 3 to 100 times higher than the commodities. A more important indicator is that the speciality polymers accounted for just over 25% of the turnover of the polymer industry in '82/'83 and by weight some 10%. It is estimated that the current growth outstrips that of commodity polymers by a factor of about 2.

SPECIALITY POLYMERS IN PROSPECT

First it is worth considering how the present industrial position has been established. We see at once two important features:

(i) Conventional polymer chemistry synthetic routes are used in every case.

(ii) Performance is usually achieved by adjusting the chemical structure in an essentially homopolymer system, i.e. by designing specific functional polymers.

Note also that most of the random copolymers or blends or grafts in the market are designed to compromise over a range of properties rather than meet a selected high performance criterion. Perhaps block copolymers offer certain exceptions in the sense that unique anisotropic properties have been demonstrated which in fact turn on the physics of processing and the ordering of the two phase structure than on functionality.

In fact the key to the expanding horizon for speciality polymers lies now in designing in with the basic chemistry of these systems a degree of physical organization at the molecular level. This can come from inherent properties due to molecular structure (e.g. liquid crystal or phase separation tendencies) or ordered polymerization environments.

Although the markets are not yet established we see from activities in Research and Development laboratories in Academie and Industry the pointers to the next generation of speciality polymers to add to the present base.

Self-orientating polymers

We have already noted the observation of incipient liquid crystal formation in the formation of Kevlar fibre. These are now two routes to self-orientated polymers which are being pursued. The first stems from older work on polymerization in the solid state in which, for example, trioname was connected to polyformaldehyde; unfortunately polymerization occurred in the liquid domains and so no significant effects were observed. Now there is some progress since Boughman showed that to retain steric control a single crystal, monomer crystals must be used which have the same density as the polymer crystal which is produced. Otherwise the change in volume destroys the selectivity of steric control.

Second, a great deal of work is being done with mesogenic groups inserted in the main polymer chain or

Table 1 Approximate selling prices of speciality polymers

	\$/lb
UHMW Polyethylene	1.0
Polyacetal	1.5
Polycarbonate	1.6
Poly(phenylene oxide)	2.0
Poly(ester carbonate)	2.5
Poly(ether imide)	4.3
Poly(ether sulphone)	4.2
PTFE	5.0
PDMS	5.5
Poly(vinylidene fluoride)	6.0
Poly(amide imide)	14.0
Poly(ether ether ketone) (aryl)	30.0
Reference: Polyethylene	0.3–0.4

in pendent side groups. Orientation effects have been demonstrated in melts and rubbers of this type and they will clearly offer the possibility of providing a new family of opto or electronically active polymers.

But the observation that some polymer structures have the capacity to be self-orienting by liquid crystal type mechanisms is likely to be the route by which a new family of self-reinforcing polymers are achieved. The polyamide fibres are the precursors but there are prospects now of self organized plastic materials which will develop high strength and offer good chemical and wear resistance.

Thin films

Another area of considerable interest is the use of Langmuir–trough-techniques to organize monomers into monomolecular arrays, from which polymerization can be initiated. An extension of this method, by means of dipping techniques enables the build up of ordered multi-layered structures prior to polymerization. Clearly there is great promise both for optically and electro active films to be made this way and additionally to offer a new dimension to the controlled synthesis of membranes. This is an area of work where the collaboration between the research team and the end user is going to be critical in developing the exploitation of the techniques.

Conducting polymers

In the early 60's most of the work on polymer conductivity was directed to abortive attempts to find conjugated structures which would provide safer conducting materials at temperatures above 4 K. In recent years this has given way to more realistic attempts to obtain polymers with conductivities approaching those of metals. Polyacetylene or polypyrrole structures have been preferred but conductivities approaching those of metallic good conductors are only achieved with the incorporation of dopants such as I₂ and SbF₅. The application for these materials has yet to develop and there is considerable need for refinement in the materials themselves but the breakthrough that has undoubtedly been achieved is to approach the conductivity of metals.

There is one continuing theme when viewing speciality polymers in prospect and that is they will be essentially organic materials prepared by the well established polymerization mechanisms, albeit now with more physical organization in the relative orientations of monomers. There is however no longer an embargo on somewhat exotic monomers since the applications envisaged often require relatively small amounts of material and can bear relatively high costs.

In addition there are two major changes in prospect. The first is that the polymer macro structure is essentially tailor-made both physically and chemically for its end use. Thus as speciality polymers are developed for micro electronic applications, for specialized optical applications including integrated optical systems or even for making components in fine instrument engineering, each product will be so closely associated with its end use that a closely integrated R & D effort will be required between the polymer supplier and device manufacturer. The second change calls for close collaboration between the polymer chemist and physicist even in the conceptual stage of polymerization and not simply in the 'end-on' sense so familiar where new polymers have been made and handed on for physical examination. Now we are likely to see the chemical physicist or physicist increasingly engaged at the polymerization stage to ensure that the full benefits of molecular organization are realized.

It is fully twenty years since such a stimulating prospect stretched before polymer scientists.

Even now I am conscious of having reviewed the prospects for bulk speciality polymers. That is because the content of this symposium concentrates on bulk

polymers. Much could be said about speciality polymers in solution taking in the special effects which distinguish linear polymers from branched polymers, flexible from stiff polymer chains, nonelectrolyte from polyelectrolyte systems, and so on. Indeed this latter subject is rarely reviewed in its own right and might form the topic for POLYMER's 50th anniversary!

Yet there are dangers in our preoccupation. The more we endeavour to develop specialized polymers the more conscious we must be not to lose sight of our past, i.e.: the synthetic routes to, the characterization of and the understanding both in phenomenological and molecular terms of assemblies of giant molecules in bulk and in solution. There is still much we do not know about the controlled synthesis of stereospecific polymers or highly branched polymers or networks. There is even more to understand about the nature of the rubber, glass and crystalline states and the documentation of polymer properties. Only by proper regard for the basic principles of connectivity as manifest in polymer science will we prevent the search for new polymers becoming an *ad hoc* scramble and maintain it as an effective intellectual pursuit in which good science begets good technology.