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HYDROCARBON POLYMERS—PERSPECTIVES

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Abstract—Factors underlying the supply of raw materials and the manufacture of petrochemical-based polymers are discussed, with particular emphasis on future trends and energy consumption. Examples are given of development in monomer synthesis, e.g. for isoprene, and of recent advances in the synthesis and properties of hydrocarbon polymers, specifically new elastomers, together with the likely technological and economic impact.

Hydrocarbon polymers are the largest volume group of synthetic polymers, totalling over 30 million tons in 1974, and constitute over half of all wholly synthetic polymers. Additionally, there are a further 3·5 million tons of *cis* 1,4-polyisoprene in the form of natural rubber.

Relatively cheap and abundant raw material sources in conjunction with ease of manufacture, good mechanical properties and environmental resistance make them "work horses" of the polymer industries.

Individual members, of course, have widely disparate properties and indeed the only common features which result from their hydrocarbon structures relate to properties such as oxidative degradation, which do have many similarities. The justification for a review of this type therefore stems from the current interest and concern with raw materials supplies and costs, and with conservation and recycling. A major portion of the review will be concerned with these aspects but, since the future of all current materials must be affected by changes in technology and the emergence of new materials, relevant developments in polymer science are dealt with also.

BASIC RAW MATERIALS

Although a figure of the order of 30 m tons/annum appears to be very large, against a total usage of carbon and hydrocarbon compounds in 1970 approaching 7000 m tons coal equivalent [1, 2] (Fig. 1) it is clearly a very small proportion. The petrochemical industry is predominantly oil/gas based and this should be considered against the steadily growing dependence on oil and gas compared with coal for all energy purposes; note particularly the change in the U.K. over the past 25 years [3] (Fig. 2). This, perhaps indicates a past trend which may be reversed in coming years, with re-emphasis on coal as a primary fuel. It is also apparent that the chemical industry of the future could be based on coal (Fig. 3) equally well as on oil or gas and, indeed, the technical bases for this were laid many years ago. Materials such as formaldehyde, methanol and ethanol could be obtained at 3–5 cents/lb from coal at $10/ton, while the processes leading to aliphatic hydrocarbons (e.g. Fischer–Tropsch synthesis) could serve as a base for many polymers. Additionally, one should refer to the

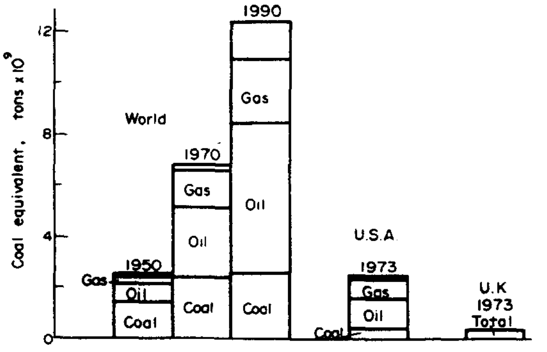

Fig. 1. 1950–1990 (est.) Energy consumption (total world, U.S.A. and U.K.).
Figures for OECD territories (representing mainly developed nations but without the Communist bloc) are something over half the world total at $3{\cdot}5 \times 10^9$ tonnes oil equivalent (1 tonne oil ≡ 1·5 tonnes coal).

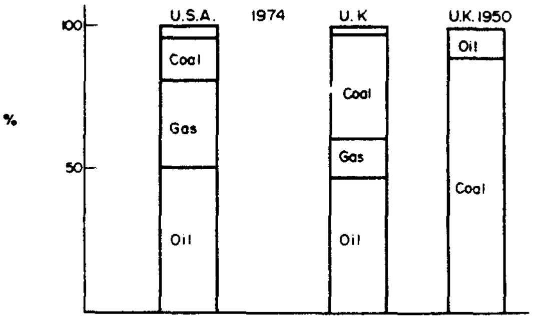

Fig. 2. Energy distribution (U.S.A. 1974; U.K. 1950, 1974).

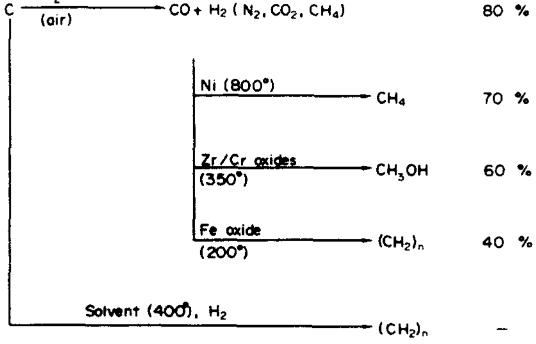

Fig. 3. Coal gasification and liquefaction.

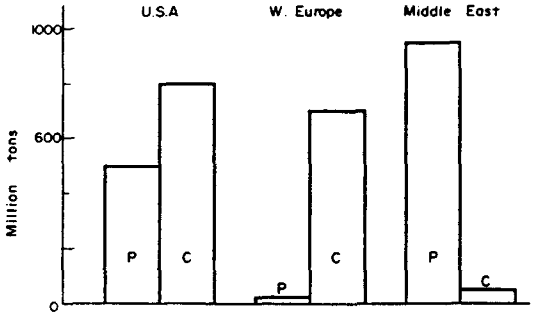

Fig. 4. Oil production (P) and Consumption (C) in U.S.A., W. Europe and Middle East (1973).

solubilization of coal at high temperatures with solvents, and by hydrogenation as a source of high quality hydrocarbons, particularly aromatic compounds. However, the main impact of the new technology will not be apparent for at least 10 yr and is likely to be aimed primarily at fuel gases so that the oil/gas raw material base for polymers is likely to dominate for some years. A major problem in this connection, of course, is the imbalance between oil production and use in different parts of the world. This is well appreciated and an extensive discussion in this review would be inappropriate. The position need only be recorded by the information in Fig. 4 showing oil production and consumption in the U.S.A., W. Europe and Middle East [4]. As a consequence of this, ultimately it seems inevitable that a major redistribution in the location of the world's petrochemical industry must occur.

The relatively minor proportion of the total oil and gas used in polymers referred to above is illustrated in two ways in Fig. 5. On the left are shown petrochemicals and polymers produced in relation to hydrocarbons consumed in the U.S.A., about 1·5% of total,* while on the right is shown the amount of crude oil used for the manufacture of a set of four tyres (including all manufacturing and processing energy) and the fuel used by the vehicle in abrading roughly 10% of the tyre weight. Another statistic illustrating the same point is that about 3% of the oil used in W. Europe is cracked for ethylene.

Two further observations can be made from this: firstly that most petrochemicals go into polymers (about three-quarters of the total) and secondly, that although polymer recycle and materials economy are important there must be far greater benefits to be made elsewhere achieving substantial economies in the use of fuel and energy. In this context it may be noted that wasted flared-off gas in 1971, mainly in the Middle East, was roughly equivalent to 220 m tons of coal in energy content [5]. This is about two-thirds of the total U.K. energy consumption, and approaches the total of oil/gas consumed by the petrochemical industry.

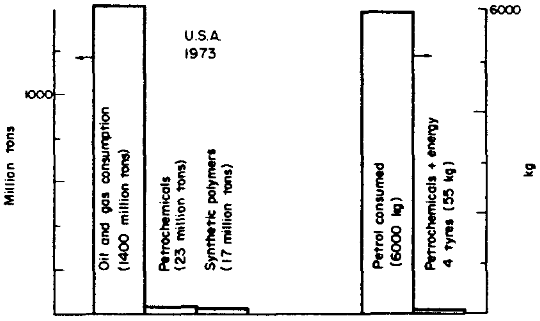

Fig. 5. Hydrocarbons for fuel and polymers.

Table 1

Product	Energy Input (MJ/kg)
Polyethylene	44
Styrene/Butadiene Rubber	71
Grain (Dry)	6
Cellulose (Crude)	0.3
Fuel	**Energy Output (MJ/kg)**
Coal	30.0
Oil (Crude)	45.0
Gas (Methane)	55.5

The energy used in polymer manufacture is not inconsiderable; Table 1 gives values for the energy inputs for the production of several polymers [6], in comparison with the energy outputs from three important fuels.

It is seen that at least an equal weight of fuel, and in some instances considerably more, is required to produce a polymer and that the energy required for synthetics is much larger than for carbohydrate production. The question may cogently be raised as to an agricultural basis for polymers. It should be appreciated, however, that in most cases some energy input would be required for conversion of carbohydrates, for example, into ethylene and butadiene and thence to polymers and the ultimate gain may not be large. This qualification should not apply to a directly produced hydrocarbon polymer, like natural rubber, where the energy required might be expected to be comparable with the above values. The output/acre, of course, is lower than that for carbohydrates and another relevant point which should be made is that the land utilized to produce 1 m tons of natural rubber could also produce sufficient food to feed 1 m people [7]. Similar arguments could presumably apply to other agriculture based polymers, including established non-hydrocarbon materials such as cellulose.

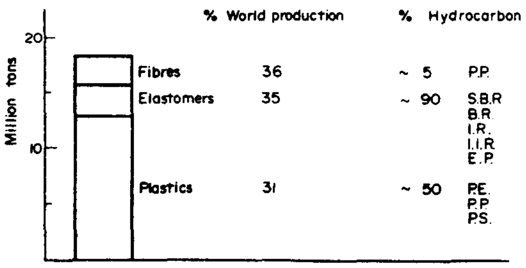

Fig. 6. Synthetic polymers production (U.S.A., 1973). (The polymers figure differs from that in Fig. 5. since total plastics production includes non-petrochemical material, e.g. cellulose-based plastics, urea in U.F. resins, coal tar and wood products).

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* The total energy consumed will be, of course, considerably larger.

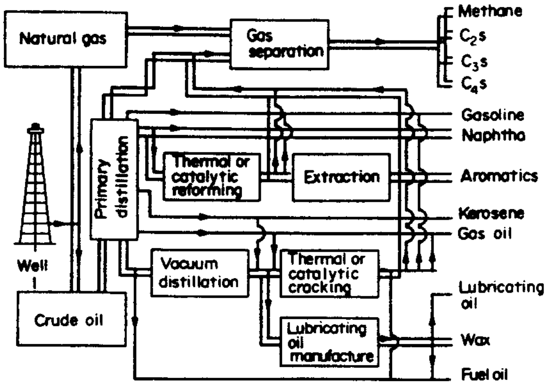


Fig. 7. Oil/gas products from refining and pyrolysis of crude oil.

Of the petrochemical based polymers, about half are hydrocarbon (Fig. 6). In the synthetic fibres they have relatively little impact, they dominate in the elastomers and the balance is fairly even amongst plastics.

They are derived, of course, from distillation, reforming and cracking of liquid petroleum or associated gases (Fig. 7), which forms part of a vast industry concerned not only with raw materials for petrochemicals but also, and primarily, with fuels for industry and transportation.

ECONOMIC FACTORS

The economics of these processes are highly complex and could not be done justice in a brief review. There are massive differences between the petrochemical industries in the U.S.A. (dominated by production of light liquid fractions for gasoline from crude oil and cracking of associated gases for ethylene, propylene, etc.) and Western Europe where the main product from crude is fuel oil, where there is little or no alkylation and much less hydrocarbon reforming for motor fuel, and where most petrochemicals are obtained mainly by naphtha/gas oil cracking. Thus, two-thirds of U.S. benzene comes from reformate compared with one-third in W. Europe, and most of the butadiene in the U.S.A. is produced from butane–butene dehydrogenation compared with extraction processes from the C4 cut of cracked naphtha in Europe and Japan. Quite apart from differences in behaviour of different sources of crude oil, it will be apparent that the supplies, balance and economic value attached to the various products will vary considerably in different territories.

Shortage of natural gas is moving the U.S.A. towards naphtha cracking but there is a natural reluctance towards this not only from the "clean" type of gas cracking reaction but also because a 5 × 10^5 ton ethylene plant from ethane would involve a capital investment much smaller than for a liquids-cracker [8]. The large number of products from the latter also mean complex and interlinked marketing operations. Some of the products from ethane and naphtha cracking are shown in Table 2.

Table 2. Ethylene manufacture

Source	Ethane	Naphtha	Crude Oil
Cracking temp.	800°C	650°C	2000°C
Ethylene %	75	26-33	33
Propylene %	3.5	13-17	4.5
C_4 %	-	4.8	3
Methane + hydrogen %	15	12-20	) 20
Heavy oil %	2	2-5	)
Pitch %	-	-	) 19

Table 3. Monomer costs (¢/lb)

	Ethylene	Propylene	Butadiene
1970	4	3	8
1974	6-8	5-7	13-16
1975	9-11	8	17-18
1977	14-17	11-13	17-19
1980	17-20	17-19	18-20

The trend, therefore, although hard to predict because of transient but severe economic fluctuations is one of continued reliance on crude oil for many years with, possibly, much later a major contribution from coal. There may be a greater tendency, because of local acute shortages of ethylene, to increase cracking severity to maximize its output—at the expense of propylene, butadiene, etc., and possibly as an extreme case—the use of crude oil directly (Table 2).

Costs, again with reservation that there will be major fluctuations in response to economic activity, are likely to rise steadily. In 1974 prices escalated rapidly but this was not only due to the increase in cost from *ca.* $2 to $9–10/barrel for crude oil but also from record industrial growth (17%) in the previous year. This latter alone would have resulted in pressure on supplies and price rises would have occurred, although obviously to a lesser extent and at a later date than what actually happened. The down-turn in industrial activity in the latter half of 1974 and in 1975 have eased pressures on many materials, exceptions being aromatic feed stocks which go mainly into motor fuels where many additional factors including lead levels and octane ratings must also be taken into account.

It appears that benzene will remain in short supply and propylene will be in greater demand, for polypropylene and within the refinery (particularly in the U.S.A.), although already new capacity has started to ease the situation [9a]. Butadiene supplies will be adequate in Europe but the shortfall in supplies in the U.S.A. (*ca.* 100,000 tons/annum for the next few years) and alternative uses in chloroprene and nylon 66 manufacture will eliminate much of the expected surplus from naphtha cracking for ethylene, mainly in W. Europe and Japan.

It is difficult to predict the relative movements in price of various feed stocks since they will depend on immediate supply and demand, but they are expected to increase, particularly if the industrial recession ends by late 1975–1976. In Table 3 are included some U.S.A. estimates for ethylene, propylene and butadiene indicating price increases throughout this decade [9b]. The position of styrene, although prices have eased recently, will be dominated by the benzene position.

The costs of polymers obviously will reflect these monomer increases and for the most part are double those of two or three years ago.

Current list prices for several hydrocarbon polymers are:

SBR 1500	360 £/tonne
BR	390
PE (LD)	300
(HD)	345
PP	320
PS	330
EPDM	410–490.

Natural rubber, as might be expected, has had large price fluctuations in the past year or so but currently is stable at £280–300/ton for first quality rubber and very competitive with the general purpose synthetic rubbers.

MONOMER SYNTHESIS

From the above, it would appear that for simpler hydrocarbons such as ethylene, propylene and butadiene there is little scope for alternatives to the existing processes from oil and gas. Styrene is currently produced from benzene via ethyl benzene or from ethylbenzene from the BTX aromatics fraction, either by dehydrogenation or co-oxidation with propylene followed by dehydration by the Halcon process. The monomer is present to the extent of 4–6% on ethylene produced by naphtha cracking, but at the present time difficulties of separation from xylenes and other similar boiling point hydrocarbons have precluded its separation directly. An extractive distillation process has now been devised [10] and gives very high purity monomer.

Of the other hydrocarbon monomers from cracked naphtha, cyclopentene (from cyclopentadiene) and the 1,3 pentadienes conceivably may come to the fore for new valuable elastomers. These latter are, of course, present in much smaller amounts and their separation in pure form more difficult and costly, and synthetic routes may become attractive. Figure 8 shows four routes for isoprene synthesis from isobutene. These processes and others, such as the propylene–dimer route, may compete successfully with the extraction process under some circumstances, for example, where the total isoprene in a C_5 stream at a refinery complex is inadequate for a polymer plant [11].

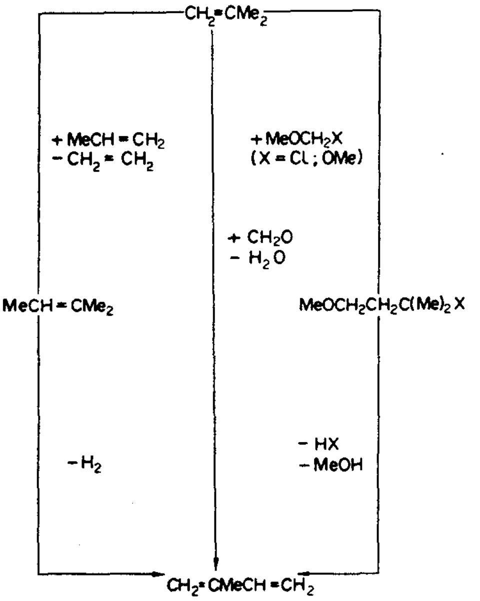


Fig. 8. Isoprene syntheses from isobutene.

Other hydrocarbon monomers of increasing interest and not directly available from naphtha are 1,4 hexadiene and 5-ethylidene-2-norbornene (used in EPDM manufacture) and norbornene.

ADVANCES IN POLYMERIZATION

Activity directed towards the polymerization of hydrocarbons, although less than in the last two decades, is likely to remain high in several areas. Greatly improved processes for the synthesis of polyethylene and polypropylene have been devised —particularly the development of highly active catalyst systems [12]. One example of these contains magnesium as an activator and gives exceptional yields of polymer (above 10^6 g/g transition metal catalyst). The reasons for this are not entirely clear but one factor is greatly increased catalyst efficiency. Normal Ziegler–Natta catalysts are generally less than 1% efficient in terms of transition metal, whereas the latest systems have 60–100% of the atoms able to initiate polymerization. The well-known supported chromic oxide catalysts are extremely active [13] and zirconium tetrabenzyl on alumina likewise gives extremely high rates [14]. Soluble catalysts in general are not particularly active and many of them, surprisingly, are of low efficiency [15].

New and effective catalyst systems continue to be found for diene polymerization and Table 4 gives recipes for two catalysts which give very high *cis* content polymer [16]. In contrast all the catalysts for high *cis* 1,4 polyisoprene are based on β $TiCl_3$, the original discovery dating from 1955–1956 although considerable improvements have been made in their efficiency [17].

From more fundamental studies, values for propagation reaction velocity coefficients in olefin polymerization are now becoming more firmly established. Although they are generally low compared with free radical systems (Table 5) [15], there are some high values, particularly for ethylene with zirconium and chromium based catalysts. The implications for high efficiency low impurity level industrial processes are obvious.

Propagation constants fall greatly with substitution at the double bond, and branching in the monomer molecule adjacent to the double bond is particularly

Table 4

Catalysts for High cis- Polybutadiene	
Butadiene (10% in hexane or benzene)	100g
Aluminium tri (isobutyl)	10^{-2} moles
Aluminium ethyl dichloride	2.5×10^{-3} moles
Cerium octoate	2.5×10^{-3} moles
Temp. 50°C, 10 hours; polymer yield 95%	
D S V 1.1; Cis 1,4 97%	
Butadiene	100g
Hexane	660 ml
Uranium (π - allyl)$_3$chloride or $U(OR)_4$	4.7×10^{-4} mole
Aluminium ethyl dichloride	1.4×10^{-4} mole
Temp. 20°C; Time 1 hour; Polymer yield 83%	
Cis 1,4; 99%; D S V 4.5	

Table 5

Propagation Velocity Constants	Propagation Coefficient
Ethylene	(1 mole^{-1} sec^{-1})
$TiCl_3$	76 (40°C); 78 (60°C)
Cp_2TiCl_2	39 (45°C); 15(10°C); 6 (0°C)
CrO_3/SiO_2-Al_2O_3	720, ~ 1000 (75°C)
$Zr(CH_2Ph)_4$	21.8×10^3 (80°C)
Propylene	
$TiCl_3$	2.8 (70°C); 5.6(70°C); 6.2(60°C)
VCl_3	9 (40°C)
4-Methyl Pentene-1	
$TiCl_3$	5 (30°C)
Butene-1	
$TiCl_3$	7 (60°C)
Butadiene	
TiI_4	2.5 (30°C)
$Ti(OR)_4$; $Ti(OR)_3Cl$	0.7 (20°C); 0.6 (-20°C)
$NiX_2/Al\ Et_3/BF_3.Et_2O$	4 (40°C)
$Ni(\pi$-$C_3H_5)OCO.CF_3$	1.2×10^{-3} (30°C)
$Cr(acac)_3/Al\ Et_3$	4.2×10^{-3} (30°C)

deleterious in its effect on rate, emphasizing the importance of steric factors in the monomer coordination step. The concept of a specific complex between monomer and catalyst is frequently advanced but possibly its significance in directing and controlling the propagation reaction may be over-emphasized. In practically all systems, reactions are first order in monomer and such data as are available show monomer adsorption coefficients on metal subhalides to be low. Thus, values of the equilibrium constants for propylene and 4-methyl pentene-l on $TiCl_3$ are *ca.* 0·1–0·2 compared with 140–220 for $AlEt_3$ and values of over 1000 for polar inhibitors.

Although the views on polymerization mechanism have not changed greatly in recent years, there have been advances particularly in the study of catalyst and propagating chain ends by techniques such as ESR and NMR with soluble catalysts for diene polymerization [18]. Nevertheless, the factors influencing such features as structural and geometric isomerism in the propagating chain are not understood.

POLYMER DEVELOPMENT

Elastomers

In elastomers a major objective has been to introduce thermoplastics processing techniques with the elimination of vulcanization. In applications where dimensional stability is required under load and at elevated temperature, progress has been very limited and hydrocarbon thermoplastic elastomers have severe limitations. Nevertheless, there have been advances and recent developments are the blend or graft EPDM/polypropylene elastomers. These have good mechanical properties and much improved temperature stability compared with the SBS types (Table 6). They still do not match, in network stability, the thermoplastic polyurethanes or the block polyether-aromatic polyester elastomers.

Table 6

Thermoplastic EPDM/Polypropylene	
Sp. G.	0.88
Hardness (Shore A)	82
Tensile strength (20°C)	8 MN/m^2
(100°C)	4 MN/m^2
E @ B	200%
100% Modulus	7 MN/m^2
Tensile set (Break)	30%
Compression set (20°C)	30%
(100°C)	70%
Resilience	50%
Flex life	250-750,000 cycles

In vulcanizable hydrocarbon elastomers, a few changes have occurred in recent years, possibly the most important industrially being the transformation of EPDM from a special purpose to a general purpose elastomer (Fig. 9) [19].

One of the more interesting of the newer elastomers is 70% *trans* polypentenamer

$$[-(CH_2)_3-CH{=}CH-]$$

obtained by ring-opening polymerization of cyclopentene by tungsten catalysts [20]. As would be expected, in its properties it is broadly similar to *cis*-polybutadiene but for reasons of more facile chain orientation it has superior self-adhesion and strength without reinforcement, and a T_g comparable with that of polyisoprene.

Of particular theoretical interest and potential practical value are the alternating copolymers of propylene and butadiene. Here the catalyst operates at low temperatures and with a specific range of catalyst compositions (typically based on VCl_4)—otherwise polypropylene or *trans* 1,4 polybutadiene are formed. It is possible that control over the propagation reaction is achieved by the possession of three coordination sites for monomer and polymer, such that at the catalyst site there alternates either one π bond and one π-allylic chain end (from the diene) or one sigma bond from the propylene end group and two π bonds from the diene monomer. Catalysts which give good yields of high molecular weight copolymer contain organo-titanium compounds such as $TiCl_3(OCOR)$ [21].

Polybutadiene of high vinyl content was the earliest to be manufactured on a significant scale but it disappeared for many years as a commercial product because of inferior resilience characteristics. It may now have a new lease of life since, owing to its higher T_g, it can have properties more akin to SBR than to the high 1,4 polybutadienes [22] and therefore more suitable for passenger car tyre treads (Table 7).

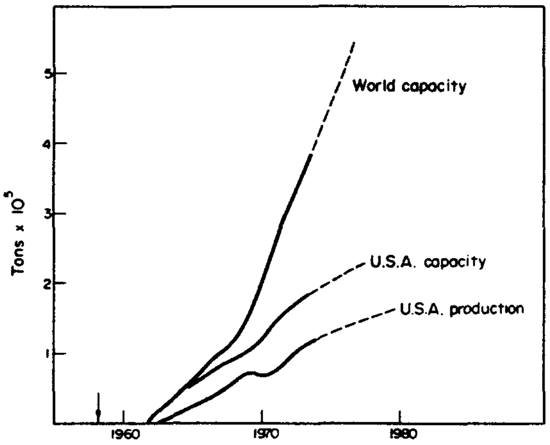
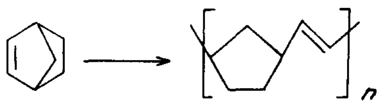


Fig. 9. EPDM capacity and production.

The production of such polymers is facilitated by the availability of the lithium alkyl catalysts where, with polar additives, it is possible to control vinyl content and hence elastomer T_g as desired.

Speciality polymers are less attractive now partly owing to high development costs and small markets but also because the existing range of materials covers most of the application requirements—except, of course, the universal demand for mutually exclusive properties. Even so, examples appear occasionally and one which is interesting is plasticized polynorbornene, where the monomer is



polymerized by ring opening rather than at the double bond. This polymer has a T_g 30–35° but, when mixed with large volumes of oil and fillers, gives an elastomer with good physical properties [24] (Table 8).

The properties are open to considerable variation but in the example given where resilience is low it would be of possible interest for damping applications.

The factors influencing properties of hydrocarbon elastomers are quite clearly defined and synthesis to achieve control of structure and adequate processability (molecular weight and molecular weight distribution, stress crystallization, etc.) and fabrication (raw polymer strength and extensibility, and autoadhesion) are fairly well understood. Likewise the theory of viscoelasticity and the analysis of such properties as crack initiation and growth, friction and abrasion in terms of molecular features such as T_g and stress crystallization and the physical processes involved are becoming much better understood [25, 26]. The relationship between strength (energy input to break, U_B) and hysteresis loss (H_B)

$$\left\{\frac{294}{(T)}\right\}^{1/3} . U_B = K(H_B)^{2/3}$$

has brought about a greater understanding of strength properties [27] in "gum" and filler reinforced vulcanizates and has drawn attention to a fundamental incompatibility between ideal elasticity and strength, at least with amorphous non-crystallizing or filled elastomers.

Table 7. Tyre road grip and elastomer T_g [23]

Elastomer	Coefficient* of Friction	Skid Value (Locked Wheels)	Polymer T_g
High (50-60%) vinyl	(0.83	0.67	-40°C
Polybutadiene	(0.80	0.63	-45°C
High *cis* Polybutadiene	0.60	0.49	-104°C
Natural Rubber	0.79	0.56	-70°C
Emulsion SBR	0.81	0.63	-51°C

* Wet asphalt.

Table 8

Polynorbornene Elastomer		
Polynorbornene	100)	
Aromatic Oil	200)	
SAF Black	200)	
Sulphur	0.5)	Cure
CBS	6)	10 min
ZnO	5)	@ 155°C
Stearic Acid	2)	
Tensile strength	14.5 MN/m^2	
100% Modulus	1.8 "	
300% Modulus	11.8 "	
Elongation at break	375%	
Hardness	65°BS	
Resilience 50°C	20%	
Low temperature stiffening	-12°C	

It may be concluded that except for deficiencies in regard to extreme service conditions (thermo-oxidative, chemical attack and solvent swelling) the hydrocarbon elastomers will remain unchallenged and the respective market shares will depend on minor technical performance/cost considerations. The stability of the position is obvious from Table 9 [28].

Fibres

In fibres, little change in the relatively minor impact of hydrocarbon polymers is foreseen. About one-third of polypropylene consumption, which is the only significant hydrocarbon fibre, is used in fibre or filament form, corresponding *ca.* 5% of all hydrocarbon polymers. Clearly where specialized requirements are needed such as low density, low water absorption and good chemical resistance, they will fulfill a need, but the rapid fall in strength with temperature, continued and extensive creep under sustained load and poor abrasion resistance are unlikely to be dramatically improved, and hence their chances of capturing a major portion of the fibre market are relatively small.

Plastics

In the plastics area, the hydrocarbon polymers are established firmly with their combination of good

Table 9. Elastomer consumption (N. American)

	Current	Estimated	
	1975	1980	1985
SBR	46.1	45.0	44.6
NR+IR	26.1	26.6	26.8
BR	11.5	10.8	10.9
IIR	4.1	4.1	4.2
EP	3.8	5.3	5.2
Total	91.6	91.8	91.7
Volume	100	118	137

properties, low cost and easy processing. Considerable scope for property improvements from changes in macrostructure resulting from process modifications in the semicrystalline polymers exists, and the effects of modifications of crystal size and structure are of significance. One well-established example is nucleated polypropylene with improved flow and optical properties.

The effects of high pressure processing (e.g. rolling, cold-forging or drawing) to give oriented materials with extremely high moduli are well known [29] and there are ingenious fabrication procedures which result in changes in morphology, e.g. crossed molecular orientation brought about by rotating the core of a mould during the polymer injection process [30]. In conventional injection moulding operations with crystallizable polymers, orientation in the melt can occur with differences in morphology in the outer skin of the sample and the inner core. The skin contains large numbers of fibril nuclei with lamellar overgrowths while the shear zone later during mould filling has lower stresses with fewer fibrils. The inner core will have the normal spherulitic structure. The proportion of skin to core falls with increasing injection temperature, and injection pressure is another variable. The result can be a marked increase in yield stress in the polymer, e.g. from 4000 psi at 70% spherulites to 5000 psi at *ca.* 20% spherulites [31].

Even in amorphous polymers such as polystyrene, considerable improvements can be achieved by mechanical processes. Thus, biaxially drawn polystyrene (3/1 at 110°) becomes tough and has improved craze resistance and impact strength. In view of recent developments suggesting considerable order in amorphous polymers [32], this may not be surprising.

CONCLUSION

Although the economic future is uncertain, whatever the materials developments of the next decade or two, the current range of hydrocarbon polymers will have a major role. New polymers are probable but it seems unlikely that there will be a repeat of the remarkable discoveries of the 1950s–1960s. Moreover, notwithstanding the great importance of hydrocarbon polymers, the position should not be overstated and their fundamental limitations must be emphasized. In general, their resistance to heat and to oxidative degradation is limited; where high temperatures and stresses and hostile environments are encountered, they do not compete with the many polar aromatic or fluorine-containing polymers. Polyaromatic hydrocarbons (e.g. poly-*p*-phenylene) are stable up to 500° and resistant to oxidation [33] but their intractable nature has greatly restricted their use. It would seem, therefore, that the future promises steady rather than spectacular advances; although the prophet is frequently confounded by events, a continuation of the types of developments discussed in this review is more probable than a major shift in direction.

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