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The Historical Development of Polyesters

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1 INTRODUCTION

Strictly speaking, the term *polyester* ought to refer to a chemical compound containing many ester groups in each molecule. In practice, however, it usually refers to polymeric materials containing ester groups as major structural components of the main chains of the macromolecules of which the polymer is composed, and this is the sense in which it is used here. The term is not now usually applied to polymers that contain ester groups attached to the main chain either directly, as in cellulose triacetate, poly(vinyl acetate) or poly(methyl acrylate), or within short side-chains.

There has in the past been some confusion in the use of the term *alkyd*, which is said to have been derived from *alcohol* plus *acid*. The definition offered by Kienle [1], discussed later, is broad enough to include all polyesters derived essentially from diols and dicarboxylic acids, and consequently linear polyesters were initially included in this class of polymer. On the other hand, Bjorksten *et al*. [2], in their 1956 compilation of published information about polyesters, restrict the term *polyester* to the polycondensation products of dicarboxylic acids with dihydroxy alcohols, and say that 'this definition does not include materials commonly known as alkyds'. At the present time, there are still problems of nomenclature in the fibre field arising from the use of *polyester* as a generic term to cover fibres containing only a very restricted range of chemical groups.

The term *ester* applies not only to products derived from carboxylic acids but also to products derived from other types of organic acid such as phosphonic or

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sulphonic acids and from inorganic acids such as phosphoric acid, and thus the term *polyester* also includes polymers containing these inorganic groups. Relatively little work has been carried out in this field, with the very important exception of nucleic acids. Polynucleotides are linear polyesters of phosphoric acid with ribose (ribonucleic acids, RNA) or with 2′-deoxyribose (deoxyribonucleic acids, DNA), and are of very high molecular weight. In both cases, purine and pyrimidine bases are attached to the pentose groups. This field is so different from the general field of polyesters that it will not be considered further here.

2 ALKYD AND RELATED RESINS

The earliest synthetic resin to be used in commerce seems to have been a polyester then termed *ester gum*, which was made by esterifying rosin (essentially an unsaturated monocarboxylic terpenoid acid, abietic acid) with glycerol. When cooked with tung oil (a glycerol ester of 9,11,13-octadecatrienoic acid), this provided varnishes that dried overnight. In this case, the polymer is formed by an addition copolymerisation process, but the product is nevertheless also a polyester.

Alkyd resins were the first polyesters to become of major commercial importance. They were originally defined as reaction products of polyhydric alcohols and resinifying carboxylic acids such as polybasic acids and their anhydrides. This definition is no longer appropriate, since it can be interpreted as including, for example, modern polyester fibres. Alkyds were first introduced into the market by the General Electric Company in the USA, whose trade mark, 'Glyptal', became an alternative name for them [3]. Earlier reports of polyester resins of this type include those from Berzelius (1847) [4], who reported a resin from tartaric acid and glycerol, Berthelot (1853) [5], who obtained a resin from glycerol and camphoric acid (*cis*-1,2,2-trimethyl-1,3-cyclopentane-dicarboxylic acid), and Van Bemmelen (1856) [6], who made glycerides of succinic acid and citric acid. The most important product of this class, i.e. the reaction product of glycerol and phthalic anhydride, was first described in 1901 by Watson Smith [7], who obtained a solid, transparent, strongly refractive resin on heating these two compounds together in a molar ratio of 2:3, and showed that a very similar product was obtained if the molar ratio was varied, even with a large excess of glycerol. He found that at temperatures above about 190 °C under vacuum the reaction mass frothed with an accompanying rise in temperature, leaving a glassy product.

According to Kienle [3], the early development work on alkyd resins was carried out between 1910 and 1915 in the laboratories of the General Electric Company. In particular, in a patent filed in 1912, Callahan [8] showed that the reaction between glycerol and phthalic anhydride should be carried out in two stages – first with the temperature being gradually raised to about 210 °C, and

then at a lower temperature of about 100 °C over a period of many hours, whose duration depends upon the dimensions of the sample. The second stage, which leads to hardening, can be carried out after coating or impregnating the material to be treated. Continuing the first stage to higher temperatures led to formation of a hard, brittle mass filled with cavities, presumably due to a combination of cross-linking (i.e. reaching the gel point) with an evolution of water vapour too rapidly for it to diffuse through the resin. Callahan believed [9] that the cavity formation was due to evolution of glycerol, but his use of a high molar ratio, i.e. 2:1, of phthalic anhydride to glycerol and the low volatility of glycerol render this unlikely. Callahan [9] then described conditions that allowed the second stage to be carried out at 200–210 °C and showed that further hardening could be obtained by continuing to heat at temperatures up to 250 °C. Other GEC patents from that period showed that it was possible to incorporate small amounts of butyric acid [10], or oleic acid [11], or castor oil [12], or both oleic acid and castor oil [13]. These were the first of many developments that extended the range of alkyd resins by giving control over the flexibility or hardness, modifying the rate of cure, and introducing the possibility of additional olefinic curing reactions, at that time referred to as 'drying'.

The main ingredients for the early alkyd resins, namely phthalic anhydride and glycerol, were already quite readily available at the time of their development. At that time, phthalic anhydride was made by catalytic oxidation of naphthalene with sulphuric acid. However, a considerable boost to the competitiveness of alkyds was the development from about 1917 of a much cheaper process for phthalic anhydride, based on catalytic vapour-phase oxidation of naphthalene.

In 1924, Kienle and Hovey began to study the kinetics of the polyesterification reaction between glycerol and phthalic anhydride. First [3] they demonstrated, among other aspects, that the reaction proceeded solely by esterification, that the initial stages were very rapid and exothermic, and that gelation occurred before esterification was complete. Further papers from Kienle and his co-workers developed a distinction between heat-non-convertible, heat-convertible, and oxygen-convertible (later element-convertible) alkyd resins. These corresponded, respectively, with the non-gelling products of a reaction between bifunctional alcohols and acids (a 2:2 reaction, where the numbers represented the 'reactivity' or functionality in ester formation of the compounds), the thermally gelling products of a reaction between reactants of the 2:3 type or higher (Figure 1.1), and the gelling products of a reaction involving unsaturated groups [1, 14]. At that time, products in the first group were not recognised as being potentially useful.

Development of the third class, i.e. unsaturated polyester resins, remained rather slow until the late 1930s, but after commercial production of maleic anhydride by catalytic oxidation of benzene began in 1933, maleic anhydride and fumaric acid rapidly became the most important sources of unsaturated groups in polyesters. The mechanism of 'drying' of these resins on their own and with the addition of drying oils (i.e. unsaturated compounds such as linseed oil) was

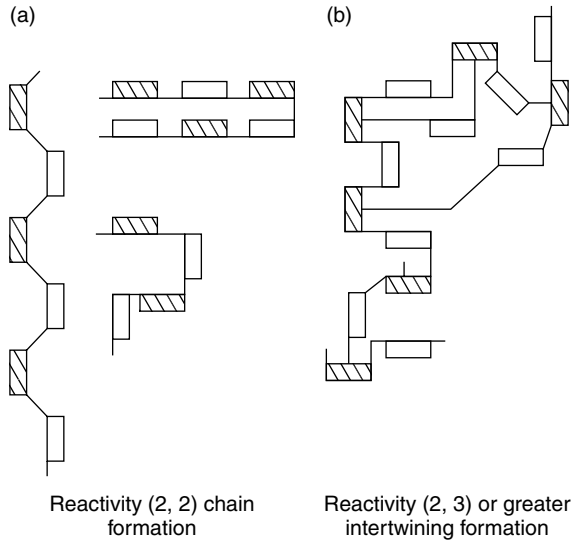

Figure 1.1 Kienle's illustration of polymer formation from (a) two bifunctional reactants and (b) one bifunctional and one trifunctional reactant [1]

investigated and, to some extent, clarified by Bradley and co-workers [15] and Vincent [16] during this period, and their 'convertibility' to insoluble, infusible structures was identified as being due to the double bonds, whose concentration in the precursors had to exceed a certain limit.

During World War II, polyesters containing unsaturated groups, particularly those based on maleic and fumaric esters with various diols, grew greatly in importance as constituents of shaped composite structures, notably in combination with glass fibres to make glass-reinforced polyesters (GRPs). The polyester was dissolved in an unsaturated monomer, commonly styrene, and copolymerisation was brought about by any of the various forms of initiation appropriate to double-bond polymerisation.

3 FIBRES FROM PARTIALLY AROMATIC POLYESTERS

3.1 EARLY WORK LEADING TO POLY(ETHYLENE TEREPHTHALATE)

In February 1928, Wallace H. Carothers (Figure 1.2), then an Instructor at Harvard, joined du Pont at Wilmington to set up a fundamental research group in organic chemistry. One of the first topics he chose was the nature of polymers, which he proposed to study by using synthetic methods. He intended to build up some very large molecules by simple and definite reactions in such a way that

Figure 1.2 Wallace H. Carothers (photograph *circa* 1930)

there could be no doubt as to their structures. If he could build up a molecule containing 300 or 400 carbon atoms and having a definitely known structure, he could study its properties and find out to what extent it resembled those of other polymeric substances already investigated [17]. The reaction between aliphatic alcohols and aliphatic carboxylic acids was one of the most fully understood condensation reactions, with very few complications from side-reactions, and suitable diols and dicarboxylic acids were available, so this was the reaction that Carothers chose for his first attack on the topic. He also noted that a study of this type of reaction should cast light on the structure of glyptals, which were already commercially important [18].

By reacting dicarboxylic acids with 5 % excess of diols, Carothers and Arvin obtained a range of polyesters with molecular weights up to about 4000 [19]. One of the collaborators in this work was J. W. Hill, who constructed a molecular still attached to a mercury diffusion pump that was capable of reducing the pressure in the reaction vessel to 10^{-5} mm of mercury [20]. He made a polyester by reacting

octadecanedioic acid with an excess of propane-1,3-diol at a temperature rising to 180 °C and then, at a reduced pressure of 1 mm, to 200 °C. He then subjected it to further reaction in the molecular still at 200 °C and a pressure below 10^{-5} mm, and thus raised the molecular weight to about 12 000 [21]. On April 30, 1930, he found that he could now pull fibres from the molten product, and that when the cooled fibres were subjected to an extensional force, they extended irreversibly at their necks to form oriented fibres of uniformly lower cross-sectional area. Carothers and Hill called this behaviour 'cold drawing' [22].

Although the acid used in this work was the 18-carbon linear dicarboxylic acid, the polymer is referred to in Reference [22] as the 3–16 ω-ester, based on the number of methylene groups in the diol and dicarboxylic acid respectively. This terminology has led to occasional confusion about the structure of these first polyester fibres, since later usage would give this polymer a code '3G18', including the carbon atoms in the carbonyl groups. This was the first 'superpolyester', or ω-ester, as Carothers named these products of high molecular weight.

Carothers and his research group synthesised many polyesters, nearly all of them aliphatic. His basic patent was filed on July 3, 1931 [23]. This work, together with his work on condensation polymers in general, proved influential in convincing the scientific community that polymers were indeed macromolecules, as maintained by Staudinger, and not assemblies of small molecules in a special state of association. Staudinger himself was initially reluctant to accept that the polyesters were polymers, since he had defined polymers in such a way as to refer solely to products of addition reactions. He thus excluded products of condensation reactions, where small molecules were eliminated as co-products of the reaction [24].

The polyesters made by Carothers and his team proved a dead end in terms of commercial development for the time being, since the majority of them had melting points too low for practical utility, and there were also problems with low hydrolytic stability. Carothers turned to other classes of polymer, including, in 1934, polyamides, which he had previously briefly explored with Hill without any success. This work led to nylon fibres – first with Coffman, to nylon 9, then with Peterson, to nylon 5,10, and then, early in 1935, with Berchet, to nylon 6,6 [17].

The first synthetic fibres to be commercialised, the chlorofibres *Pe-Ce* and *Vinyon* and the polyamides nylon 6,6 and *Perlon L* (nylon 6), all appeared in the mid to late 1930s. In 1940, ICI and Courtaulds formed a jointly owned company in the UK to make and sell nylon 6,6 under licence from du Pont. This was the situation when, in 1940, a research programme began at the laboratories of the Calico Printers Association (CPA) in Accrington, UK, which was aimed at making a polyester from ethylene glycol and terephthalic acid. The programme was initiated by J. R. Whinfield, who had been greatly influenced by a period of training nearly twenty years earlier in the laboratories of C. F. Cross, inventor of viscose, and by reading the papers published by Carothers. Whinfield asked J. T. Dickson (Figure 1.3), who had just joined CPA in 1940 from his Ph.D.

Figure 1.3 J. R. Whinfield (left) and J. T. Dickson (right) re-enact the discovery of fibre-forming poly(ethylene terephthalate) [30] (photograph *circa* 1942)

studies at the University of Edinburgh, to carry out the work. Success came quickly, and the first patent application was filed on July 29, 1941 [25–27].

Early in 1942, the discovery was brought to the attention of the British Ministry of Supply, who arranged for further experimental work to be carried out at the government's Chemical Research Laboratory at Teddington, near London. This work was carried out by D. V. N. Hardy [28], who scaled up production of polymer to a metal autoclave giving a theoretical yield of about 600 g of polymer per batch. He also set up a simple form of continuous-filament melt spinning and drawing, and attained very encouraging tensile properties (specific strength of 4.95 g/denier and extension at break of 11.8 %). In December 1943, ICI was told about the discovery and the development, and was invited to negotiate with CPA to take over further work on the topic [28–30]. At that time, ICI and du Pont had in place an agreement to exchange research results, and accordingly ICI disclosed this information to du Pont in July 1944. When ICI subsequently supplied samples to du Pont in February 1945, du Pont had already made rapid progress, due particularly to their discovery of an improved catalyst. Subsequently, in February 1947, ICI acquired the worldwide rights from CPA on a royalty basis, with the exception of the USA, where du Pont had acquired the patent rights outright

from CPA in August 1946. The US patent was therefore issued to du Pont, with a number of additional examples that are not in the UK patent [31].

According to Ludewig [32], the use of terephthalic acid for the development of polyester fibres was implemented almost at the same time by Schlack and by Whinfield and Dickson. Schlack, who had already been responsible for the development of nylon 6 fibres, directed his attention mainly to polyesters produced from terephthalic acid and 1,4-butanediol. Schlack's patent [32, 33] was not filed until 2 July, 1942, well after that of Whinfield and Dickson. This describes the preparation of crystalline oligomeric poly(1,4-butylene terephthalate) from butane-1,4-diol and terephthaloyl chloride under conditions that should give a degree of polymerisation (DP) of at most 9 (not high enough for fibre formation), and their reaction with aromatic diisocyanates to produce melt-spinnable polyesterurethanes. These products had melting points in the range 201 to 208 °C, which were due to the polyester crystallites, but the polymers were, of course, of a different chemical class from those claimed by Whinfield and Dickson. However, the BIOS report [34] of a British team on wartime textile research in Germany records that Schlack carried out an ester-producing polycondensation that gave a spinnable product which on cold-drawing gave strong fibres. Schlack himself [35] confirmed this later.

In 1953, E. F. Izard of du Pont was awarded the Schoellkopf Medal of the American Chemical Society. The report [36] of this award states that 'work on the development of a hydrolytically stable polyester was started by Dr Izard in 1944, and it led in a comparatively short time to the discovery of polyethylene terephthalate'. The report recognises that 'polyethylene terephthalate was earlier discovered independently in England by J. R. Whinfield'. Izard himself says [37] that the duPont research programme led immediately to the discovery of poly(ethylene terephthalate) (PET), which suggests that detailed information from ICI about the structure of the new fibre had not yet reached him by that time.

3.2 SPREAD OF POLYESTER FIBRE PRODUCTION

In the early days of polyester fibre development, du Pont possessed the Whinfield and Dickson patent in the USA, and while its monopoly lasted no other company could enter that market. ICI possessed licence rights for the rest of the world, and took the view that it could not exploit all of these markets on its own as effectively as if it sub-licensed to other companies in major markets outside of the UK. The first sub-licences were granted to Algemene Kunstzijde Unie (AKU) (*Terlenka*) in the Netherlands, Societé Rhodiaceta (*Tergal*) in France, Vereinigte Glanzstoff-Fabriken (*Diolen*) and Farbwerke Hoechst (*Trevira*) in Germany, and Società Rhodiatoce (*Terital*) in Italy. The first plant in France was built at Besançon, a city closely associated with the first production of a manufactured fibre by Chardonnet. ICI itself set up manufacturing facilities in Canada, where a subsidiary, Canadian Industries Ltd (CIL), was already

established and the UK name *Terylene* was adopted. Soon thereafter, licences were granted to Teikoku Jinzo Kenshi (now Teijin) and Toyo Rayon (Toray) in Japan, where both companies used the name *Tetoron* for the product [38].

This widespread sub-licensing by ICI reduced the incentive to develop a patent-free product in most of the major industrialised countries. The US market, however, was potentially so large that inevitably other large companies looked for polyester fibres that fell outside the scope of the patent now owned by du Pont. Only one such product was commercialised within the life of that patent. This was a fibre produced from poly(cyclohexane-1,4-dimethylene terephthalate), patented by Kodak [39]. This polymer was made from dimethyl terephthalate and 1,4-di(hydroxymethyl)cyclohexane, a diol that Kodak synthesised by a two-stage hydrogenation of dimethyl terephthalate, with the first stage being hydrogenation of the ring and the second hydrogenation of the ester groups to hydroxymethyl groups. Both of these hydrogenation products consist of mixtures of two isomers, *cis* and *trans*. The *cis*:*trans* ratio in the commercial polymer was approximately 2:1. This fibre was marketed in the USA from 1958 under the trade name *Kodel*, and later in Germany by Faserwerke Hüls as *Vestan*. Its properties differed significantly in many respects from those of PET fibres. For example, its melting and glass transition temperatures were considerably higher, and its density was about 12 % lower – a property that helped to offset the higher materials cost by improving the covering power.

Other US companies chose to await expiration of the Whinfield and Dickson patent before entering the market. One of the earliest to become involved was Celanese Corporation, whose joint venture with ICI, named Fiber Industries Inc. (FII; *Fortrel*), began construction of its first PET plant in 1959. Beaunit (*Vycron*) was also an early entrant, initially with a copolymer fibre that was arguably not covered by the basic patent, using polymer from Goodyear.

Thereafter, polyester fibre manufacture spread very rapidly throughout the world. Initially, the technology transfer was mainly from the existing producers, but after expiry of the patents it was provided increasingly by engineering firms, who provided not only specific sections of production plant but also 'turnkey' plants with start-up support, thus enabling relatively undeveloped countries to establish fibre production.

Many other semi-aromatic polyesters were evaluated and patented in the period immediately following the invention of PET. Some gave excellent fibres and other shaped products, with property advantages over PET, but in general the intermediates were more expensive and the polymers were not commercialised at that time. Poly(*p*-ethyleneoxybenzoate) (*A-Tell*) production began in 1967 in Japan, but the product struggled to compete. Poly(1,4-butylene terephthalate) (PBT) has proved more successful as a moulding polymer than as a fibre. Recent advances in the synthesis of naphthalene-2,6-dicarboxylic acid and of propane-1,3-diol have encouraged re-evaluation of polyesters based upon them, as described in later chapters in this book.

3.3 INTERMEDIATES

When poly(ethylene terephthalate) fibres were invented, and for the first few years thereafter, terephthalic acid and its esters were only available in small amounts and were correspondingly expensive. Whinfield and Dickson, and also Hardy [28] in the first stages of his scale-up work during the period 1942–1944, made the acid by dehydrogenating dipentene (*dl*-$\Delta^{1:8}$-*p*-menthadiene) with sulphur to form *p*-cymene (*p*-isopropyltoluene), which they oxidised in two stages, first with dilute nitric acid, and then with alkaline permanganate. The first commercially viable route was through oxidation of *p*-xylene under pressure using dilute nitric acid. The product contained coloured and colour-forming impurities that could not be removed, so it was necessary to esterify it with methanol to form dimethyl terephthalate (DMT), which still required successive recrystallisation and distillation to bring it to an acceptable state of purity. For the first few years of PET production, the polymer was all made by an ester interchange route from DMT.

An alternative route to DMT was introduced in 1953. This was based on air oxidation of *p*-xylene to *p*-toluic acid, which was esterified by methanol to form methyl *p*-toluate, which was oxidised by air to monomethyl terephthalate [40], which in turn was esterified by methanol to make DMT. The two oxidations could be combined so that *p*-xylene and methyl p-toluate were oxidised in the same vessel, and so could the two esterifications [41]. The process was due to Katzschmann of Imhausen, a firm based at Witten and later known as Chemische Werke Witten. This process, known variously by its inventor's name and by various combinations of the names of the companies involved in its development, i.e. Hercules, Imhausen, Witten, and Dynamit Nobel, rapidly replaced the rather unsatisfactory and sometimes hazardous nitric acid oxidation route to DMT.

Meanwhile attempts to find an air oxidation route directly from *p*-xylene to terephthalic acid (TA) continued to founder on the relatively high resistance to oxidation of the *p*-toluic acid which was first formed. This hurdle was overcome by the discovery of bromide-controlled air oxidation in 1955 by the Mid-Century Corporation [42, 43] and ICI, with the same patent application date. The Mid-Century process was bought and developed by Standard Oil of Indiana (Amoco), with some input from ICI. The process adopted used acetic acid as solvent, oxygen as oxidant, a temperature of about 200 °C, and a combination of cobalt, manganese and bromide ions as catalyst. Amoco also incorporated a purification of the TA by recrystallisation, with simultaneous catalytic hydrogenation of impurities, from water at about 250 °C [44]. This process allowed development of a route to polyester from purified terephthalic acid (PTA) by direct esterification, which has since become more widely used than the process using DMT.

Several other novel processes for manufacturing TA have been patented, and some of them have been used commercially, but these two remain the most important.

3.4 CONTINUOUS POLYMERISATION

Du Pont were already working on a process for continuous polymerisation of PET in 1952 and commercialised this in an early plant [45]. However, until 1963 most PET was made by a discontinuous polymerisation process. In 1962, the engineering firm Hans J. Zimmer, as it then was, started to develop an integrated continuous ester interchange and polycondensation process [46]. This process was described in 1965, by which time a plant producing three tons per day of polymer was in operation [47]. The advent of processes for pure TA led to parallel development, started in 1966, of a continuous process in which the first stage was direct esterification of TA, based on Mobil technology. Vickers-Zimmer was one of the leaders in developing methods of handling the final stages of polymerisation, where the molten polymer was highly viscous, yet it was essential to minimise the diffusion path to the polymer surface. Their discring reactor was one of several devices designed to deal with these requirements, and the resulting system was capable of producing polymer of intrinsic viscosity as high as 1.0 [48].

3.5 SOLID-PHASE POLYMERISATION

Since the tensile properties obtainable from synthetic fibres are in general superior the higher the molecular weight of the polymer, there was a considerable incentive to find methods of raising the molecular weight of polyesters beyond those readily obtainable by melt polymerisation. Some of the most valuable potential outlets for PET lay in the field of technical textiles, where uses such as tyre cords would benefit from the higher work to break. The limitations of melt polymerisation were due to the reversibility of the polymerisation reaction, which made the rate of glycol removal rate-determining for the later stages of the reaction, and also to the degradation reactions that became increasingly important at the higher reaction temperatures used to reduce the melt viscosity. Although solid-phase polymerisation involved additional handling stages, it was a potentially attractive means of overcoming these difficulties. It introduced difficulties of its own, since polymerisation rates are higher the smaller the particle size, due to the shorter diffusion path [49, 50], but conversion of molten polymer to chip is much easier than to fine particles. In addition, it is necessary to crystallise the solidified polymer before heating it to polymerisation temperatures in order to avoid coalescence of the particles, although further crystallisation during the polymerisation process permits use of temperatures above the normal melting point of PET [51, 52]. Originally developed for the production of fibres for high-performance technical textiles, solid-phase polymerisation has become particularly useful in the manufacture of PET bottles.

3.6 END-USE DEVELOPMENT

The relatively high modulus of PET fibre played a large part in making it suitable for blending in staple-fibre form with both cotton and wool, thus producing fabrics that in some respects were superior to those made from unblended fibres. Pleat retention was an important property. Some dyers considered the new fibre to be undyeable, but rapid progress was made in producing new dyestuffs and in accelerating the rate of dyeing, first by the use of carriers in the dyebath and then through the introduction of pressure dyeing at temperatures of the order of 130 °C. Continuous filament yarns were introduced, and methods of texturing them, initially adapted from those already in use for nylon, were developed. Industrial uses, such as tyre cord, made rapid progress, although problems such as adhesion to rubber had to be solved. Variants, such as basic dyeable, pill-resistant, and high shrinkage products were brought onto the market. PET proved the most versatile of all synthetic fibres, and since its materials cost basis was more favourable than that of its competitors, other than the less versatile polyolefins, it rapidly became much the most important in volume terms. Its main deficiencies are relatively poor recovery from strains greater than about 5 %, and correspondingly poor fatigue resistance.

Marketing by brand name remained important in most sectors until about 1970. A particularly interesting example is the trade name *Crimplene*, which was introduced by ICI in 1959 to describe a bulked continuous-filament polyester yarn made by a process due initially to Nava and Ruffini, who worked at the firm of Cheslene and Crepes in Macclesfield, Cheshire, in the UK. Their patents, filed in 1957–1958 [53, 54], describe a process that consists of false-twisting a continuous-filament yarn, partially heat-setting the yarn without making the crimp permanent, over-feeding the yarn onto a package to produce partial relaxation, and then heat setting, preferably using steam. The earlier patent is directed particularly at nylon yarns, but the later one concentrates on polyester. In the *Crimplene* process as promoted by ICI, the final setting was carried out on a soft wind-up package using steam in an autoclave, typically at about 130 °C. Initially commercial progress was slow, but a move in 1962 to fabrics having more attractive surface appearance led to a rapid increase in sales and profits [55, 56]. ICI licensed this process to selected customers, who became known as the 'Crimplene Club'. *Crimplene* was highly profitable from 1964 to 1971, but then it suddenly became a liability. Towards the end of its profitable life, it had the highest recognition factor of any trademark in the UK, but it had acquired a dowdy image. In August 1971, the USA imposed a surcharge on imports of polyester continuous-filament yarn. This immediately created overcapacity in the rest of the world, and a collapse in prices. Moreover, the process was slow and expensive. Rapid advances in simultaneous draw-texturing processes in the early 1970s led to a new and much cheaper type of textured yarn, and provided a final 'nail in the coffin'.

3.7 HIGH-SPEED SPINNING

At quite an early stage in the development of polyester and nylon fibres, it was recognised that there might be significant benefits in raising spinning speeds and thus obtaining higher throughput at that stage, particularly if the need for a subsequent orientational drawing process could thus be eliminated. In 1950, du Pont filed two patents disclosing the invention by H. H. Hebeler of high-speed spinning processes specifically for polyester yarns [57]. One of them claimed the use of a spinning speed, defined as the speed attained after the yarn had solidified, in the range of from 3000 to 5200 yd/min (2743 to 4755 m/min). The product was found to crimp spontaneously on thermal relaxation to give wool-like resilience, but it is doubtful whether such a process could be commercialised. The other patent claimed the use of a spinning speed of 5200 yd/min (4755 m/min) or above. The highest speed exemplified was 6350 yd/min (5806 m/min). These speeds were said to be obtainable by using a driven bobbin, a high-speed pirn take-up, or an air jet, which could be used as a forwarding and tensioning device for delivering the yarn directly to a staple cutter. This patent clearly envisaged that the products would not require any further orientation by drawing, and illustrated the production of yarns having tenacities in the range 3.2 to 4.6 g/denier and shrinkages in boiling water of 2 to 4 %. The elongations to break, however, were in the range 38 to 72 %, and so the higher-modulus fibres preferred for many outlets were evidently not available by this route. These two patents were rather ahead of their time. The engineering of high-speed wind-ups reliable enough to be used in regular production did not occur until the early 1970s, when machines operating at up to 4000 m/min became generally available through engineering firms such as Barmag and IWK, and wind-ups for still higher speeds followed a little later [58].

Spinning at wind-up speeds such as 3000 to 4000 m/min gave spun yarns that possessed higher orientation and crystallinity than those previously available, and which could also be further crystallised at temperatures lower by about 30 °C than the yarns of very low orientation (LOYs) and crystallinity obtained from the established low-speed spinning processes. They were sufficiently stable to be stored and transported without structural or dimensional changes taking place, and were therefore suitable feedstocks for simultaneous draw-texturing and draw-warping processes. This type of product, known as POY (Partially Oriented Yarn or Pre-Oriented Yarn), rapidly became a major product. At the same time, new devices for texturing POY were developed, of which the most important were friction-twisting devices based on aggregates of intermeshing discs. These displaced existing pin-twisting devices because they gave very much higher rates of false-twist insertion and hence a much increased productivity.

The further step up to 6000 m/min or more led to flat yarns that were sufficiently oriented and crystalline, of sufficiently low extension to break, and of sufficiently high tenacity to be used for many purposes without further drawing.

These FOY (Fully Oriented Yarn) products therefore eliminated the need for separate spinning and drawing stages, although not for all uses. In particular, the highest tenacity and modulus are best approached by a LOY plus high draw ratio route.

3.8 ULTRA-FINE FIBRES

The introduction of ultra-fine fibres was not solely a polyester phenomenon, although polyester was the fibre most involved. Okamoto of Toray, who was a leader in this development, defines an ultra-fine fibre as a fibre of less than 0.7 denier [59]. The word microfibre, which covers essentially the same products, is usually defined as a fibre of less than 1 decitex (=0.9 denier). These products were developed in Japan from the late 1960s, primarily to improve the hand of fabrics by reducing the bending and torsional stiffness of their constituent fibres. The earliest products to reach the market were non-woven suede-like fabrics such as Toray's *Ecsaine*. The technology was expensive, since for most products it involved extrusion of bicomponent fibres, either of the 'side–side' type, with subsequent splitting by flexing or other mechanical means, or even more effectively the 'islands-in-the sea' type, where the 'sea' polymer could be dissolved away leaving the 'islands' as extremely fine fibres. The bicomponent fibres could be subjected to normal textile processing before generating the microfibres. Moreover, the interest in improved hand and the recognition of its value in the market led to renewed attention to the direct spinning of fibres of low linear density, mostly of about 1 decitex, although products can be made in a range down to about 0.1 decitex. These products have done much to improve the image of polyester and synthetic fibres in general.

4 OTHER USES FOR SEMI-AROMATIC POLYESTERS

4.1 FILMS

The companies first involved in fibre manufacture recognised the potential value of poly(ethylene terephthalate) in films from a very early stage. *Mylar* (duPont), *Melinex* (ICI), and *Celanar* (Celanese) were among the products that entered the field first. The basic technology of film formation by melt extrusion processes is not confined to polyester film, although there are special processing features due mainly to the relatively high T_m and T_g values of poly(ethylene terephthalate) [60]. Early products were mainly rigid film that took advantage of the high modulus and high thermal deformation temperature. More recently, cast films and thermoformed packaging have become important, and co-extrusion lines have been introduced for the latter type of product.

4.2 MOULDING PRODUCTS

PET was evaluated in its early days as a moulding polymer, particularly for injection moulding. It was not very successful, because of its low crystallisation rate. Even when using a hot mould system, with mould temperatures that maximised the rate of crystallisation, the product morphology was difficult to control and the production rates were low. Attempts were made to increase the crystallisation rate, for example, by incorporating a crystallisation-promoting liquid such as benzophenone together with a small amount of a finely divided nucleating agent [61]. Early products were *Arnite*, from Akzo, and *Rynite*, from du Pont. Poly(1,4-butylene terephthalate) was marketed as a moulding polymer in 1970 by the Celanese Corporation (*Celanex*), followed by numerous other producers [62]. Its rapid crystallisation rate made it much more suitable for moulding than PET, and it proved very successful both unfilled and filled with glass fibre. In 1987, the polymer already used in manufacturing *Kodel* fibre, together with some of its copolymeric variants, was also introduced by Eastman Kodak under the name *Ektar*, later *Thermx PCT*, as a moulding product with higher thermal stability than other polyesters.

4.3 BOTTLES

In 1970, du Pont filed a patent application that proved to be the foundation stone of a major new use for PET. Two US patents resulted in 1973, with one covering 'a hollow, biaxially oriented, thermoplastic article, prepared from PET', and the other claiming a process and apparatus for preparing such an article [63]. The process was based on moulding a hollow cylindrical-shaped preform or parison (a term from the glass industry), which was then subjected to a stretch blow-moulding process involving application of internal air pressure. This led to expansion of the structure to the final dimensions, with development of biaxial orientation. Du Pont chose not to embark on bottle production itself, but instead to license the product to others. The rate of growth of polyester bottle production was very high, particularly in the more industrialised countries, and bottles rapidly became second in importance only to fibres as a market for polyester materials.

An early problem was that the blowing process as originally developed produced rounded bases, and so the bottles could not be stacked upright on shelves. Initially, bottles were equipped with separately moulded base cups, usually made from polyolefin and readily attached by a snap-on or glue-on process. The Continental Group then introduced in the USA a bottle with a shaped multilobal bottom that did not require a base cup, and further designs have followed [64].

Among the controlling factors in the production of bottles from PET are the molecular weight of the polymer and the draw ratio applied. The molecular weight required is in general higher than that of the polymer manufactured for

standard fibre products, and is higher the smaller the bottle size. The draw ratio must exceed the natural draw ratio, which is lower the lower the stretching temperature and the higher the molecular weight [65]. Particularly high draw ratios are needed for products that can maintain their dimensional stability where the pressure within the bottle is high.

Two processes have been developed – the single-stage process due to the Nissei Corporation in Japan, where both injection moulding and bottle blowing are conducted on the same machine, and the two-stage process, where preforms are made on an injection moulding unit and transferred to a stretch blowing unit, not necessarily on the same site, where they must be re-heated before stretching [66]. The need for higher molecular weights has led to increased use of solid-phase polymerisation techniques, which have the further advantage over melt-polymerised polymers that they give much lower acetaldehyde contents in the product [62].

5 LIQUID-CRYSTALLINE POLYESTERS

In 1956, Flory published two papers about the theoretical criteria for formation of a single anisotropic phase in solutions of rigid and semi-flexible polymers [67]. The theory can also be interpreted as applying to polymers where the solvent concentration is zero, in which case any anisotropic phase would become thermotropic. No thermotropic systems based on main-chain rigidity were identified until the mid-1970s, when Jackson and co-workers at Eastman Kodak [68], Schaefgen and colleagues at duPont [69], and Roviello and Sirigu in Italy [70] identified thermotropic liquid-crystalline polyesters of different structural types. It then emerged that some of the polymers described earlier in patents from the Carborundum Company (Economy and colleagues) [71] were thermotropic liquid-crystalline polyesters, although this property was not identified at the time. Still earlier patents from ICI (Goodman and colleagues) [72] described, among other things, the synthesis of aromatic polyesters that were based upon asymmetrically substituted *p*-phenylene groups and included compositions that gave thermotropic anisotropic phase behaviour, but here too the nature of this phase was not identified.

Aromatic polyesters were particularly good candidates for this new field of thermotropic main-chain polymers, since the relatively low energy of association of the ester groups led to low inter-chain forces. Further research led to the discovery that incorporation of 2,6-naphthylene or of 4,4′-biphenylyl groups, in addition to *p*-phenylene groups, as components of aromatic polyesters, introduced a useful new degree of randomness. Particularly useful, and the basis of the commercial products *Vectra* (polymer) and *Vectran* (fibre) from Hoechst-Celanese and Kuraray, are the copolymers formed by polymerisation of mixtures of *p*-acetoxybenzoic acid and 6-acetoxy-2-naphthoic acid. Within a range of

molar compositions from 75/25 to 40/60 they are readily melt-processable [73]. Polyesters of the Carborundum type became the basis of the commercial product *Xydar* (Dart Corporation, later Amoco).

6 POLYESTERS AS COMPONENTS OF ELASTOMERS

The use of polyesters in the development of elastomeric products began in Germany with the *Vulcollan* series of polymers from I. G. Farben (post-war by Farbenfabriken Bayer) [74]. The first products were typically based on hydroxyl-ended polyesters made from adipic acid and a small excess of ethylene glycol, which were then reacted with naphthalenic diisocyanates to lengthen the chains and to cap them with isocyanate groups. These isocyanate-ended polymers were chain-extended by a coupling reaction with water or other reagents, usually difunctional, such as diamines. Cross-linking by formation of biuret groups was then thermally induced to produce the final elastomeric polyester-urethane in the required shape and situation. Many other polyester-diols have since been found to be useful. Other companies that produced products of similar types included Goodyear (*Chemigum*) and ICI (*Vulcaprene*), some of which were made from aliphatic polyesteramides rather than from polymers based solely on ester linkages.

Flexible foams based on polyesterurethanes were introduced in the mid-1950s. There are now three main types, i.e. flexible, rigid and structural. The flexible type was based on aliphatic polyester-diols; rigidity can be increased by using aromatic polyester-diols, by increasing the degree of branching in the polyester, and by increasing the urethane content, and hence the degree of biuret cross-linking.

Elastomeric fibres based upon both polyester-urethane and polyether-urethane structures followed. The early work by Bayer led to the use of highly polar solvents such as dimethyl formamide. Formation of fibres by reactive spinning, where the isocyanate-ended polymer is extruded into an aqueous solution of a chain-coupling agent, was described in 1949 [75] and by dry-spinning a solution of the chain-coupled polymer in 1951 [76]. However, Bayer did not immediately use their technology to produce commercial fibres [77].

Following the introduction in the USA of *Vyrene* (US Rubber) in 1958 and of *Lycra* (du Pont; *Fiber K*, 1959, *Lycra*, 1962), many producers entered the field. In 1964, Bayer started production of *Dorlastan*, a dry-spun elastomeric fibre based on a polyester soft segment and a urethane/urea hard segment produced using diphenylmethane-4,4′-diisocyanate for chain extension and a dihydrazide as coupling agent [78]. Among the other companies involved, two, i.e. Asahi Kasei in Japan and Fillatice (*Lynel*) in Italy, used polycaprolactone as the polyester soft segment. Fujibo in Japan and Fillatice used wet-spinning techniques to make their polyester-based elastomeric fibres [79]. Polyether-based fibres, however, now dominate the market.

The elastomeric possibilities of copolyesters based upon PET (2GT) were studied at an early stage in the development of the fibre. Random copolymers with ester repeating units derived from aliphatic dicarboxylic acids containing a relatively large number of methylene groups, notably 2G9 from azelaic (nonanedioic) acid and 2G10 from sebacic (decanedioic) acid, were found to have values of T_g at or below typical room temperatures when the copolymer contained 40 to 70 mol % of units derived from the aliphatic acid. These polymers could be melt-spun and drawn to give elastic yarns, with extensions to break as high as 300 % and recoveries from 100 % extension as high as 96 %, but with low melting temperatures [80]. Melt-blending 2GT and 2G10 for a limited period of time, so that a block copolymeric structure was produced, gave better elastic properties and higher melting temperatures. In ICI, Coleman showed that block copolymers could be made by replacing part of the ethylene glycol by a substantial wt % of a polyether, polyethylene glycol (polyoxyethylene diol; PEG), with very little depression of the melting point of the polyester, since the depression is a function of the mol % of comonomer [81, 82]. However, Coleman did not extend the proportion of PEG beyond 30 wt %. Charch and Shivers, at du Pont, studied the complete spectrum of compositions, and established that elastic properties were obtained in the range 40 to 70 wt % of PEG, that the best results were obtained using PEG of molecular weight 4000, and that these products gave higher melting temperatures, higher elongations to break, and lower values of short-term stress decay than any of the previous elastomeric polyesters [83].

This work did not lead immediately to commercial elastomers, but its identification of the importance of block copolymeric structures in the field of melt-processable elastomers laid the foundation for later commercialisation of products based largely on the polyester and polyether units containing four-carbon instead of two-carbon sequences. These block copolymers of 4GT with polyoxytetramethylene diol possess superior properties in that the 4GT blocks crystallise much more readily than the 2GT blocks, the molar depression of melting point is lower for 4GT than for 2GT, and the dioxytetramethylene units present in both the polyether and the polyester possess conformational energy properties more suited than dioxyethylene units to loss-free recovery of the original dimensions after distortion. Products based on this technology were introduced as moulding grades from the early 1970s, and included *Hytrel* (du Pont), *Riteflex* (Celanese), and *Arnitel* (Akzo).

7 SURFACE-ACTIVE AGENTS

One of the problems encountered in early polyester fibre processing was that the sizes generally used with other classes of fibre to protect yarns, particularly warp yarns, against damage during weaving were not sufficiently adherent to the yarn. ICI found a surface treatment that would improve the adhesion of sizes to

polyester fibres which involved converting a polyether (polyethylene glycol) to its alkoxide anion and reacting this with the fibre surface. This process formed a di-block polyester/polyether, with the polyester block lying within the fibre and the polyether block lying on the surface, to which it provided hydrophilic properties. The process was not commercially viable, but it was then found that certain multi-block copolyetheresters formed dispersions in water that could be applied to polyester yarns or fabrics by 'pad-bake' techniques. Provided that the polyester blocks were long enough to crystallise, this treatment gave excellent hydrophilic surface properties [84]. These properties were durable towards washing, particularly if the polyester blocks consisted of the same repeating units as the fibre.

This product therefore solved more important problems than the original target, since it improved the washability and resistance to electrostatic charge development of polyester fabrics. It was marketed first by ICI in Europe as *Permalose* and in the USA as *Milease*; other companies produced similar products. Moreover, aqueous dispersions of this type of surface-active agent proved useful as rinse additives for washing hydrophobic fibres in general and became ingredients of consumer-oriented products.

8 ABSORBABLE FIBRES

Two of the deficiencies of the aliphatic polyester fibres made by Carothers were their poor hydrolytic stability and their low melting temperatures. One aliphatic polyester that had already been made many years earlier [85] by polymerisation of glycolide, the cyclic dimer of hydroxyacetic (glycolic) acid, melted at about 225 °C, quite high enough for commercial use, but these fibres had even lower hydrolytic stability than the polyesters made by Carothers. In 1963, however, American Cyanamid filed a patent application in the USA that claimed absorbable articles, particularly medical sutures, made from polyhydroxyacetic ester (i.e. polyglycolide) [86]. The Davis and Geck division of American Cyanamid made a virtue of this deficiency by manufacturing polyglycolide fibres, which they named *Dexon*, for use as absorbable sutures. The sutures were strong and flexible enough to be used in place of the sutures then normally in use, most of which remained in the body long after there was any surgical need for them, so that often a further operation was required to remove them. Some, made from catgut or collagen, were slowly and rather uncontrollably absorbed through attack by cellular enzymes. These new absorbable polyester sutures, on the other hand, hydrolysed in the body over a period of days or weeks to form harmless products.

An interesting legal case ensued in the English High Court [87], where Ethicon (Johnson & Johnson) maintained, among other things, that the formation and hydrolytic behaviour of polyglycolide fibres were already known and that it was therefore obvious to use the material as an absorbable suture. The outcome was basically favourable to American Cyanamid.

Meanwhile Ethicon (and others) developed alternative absorbable surgical sutures, based, for example, on copolymers of polyglycolide with poly-L-lactide or poly(trimethylene carbonate), and on polydioxanone, and on poly(ε-oxycaproate), and also on copolymers of these with polyglycolide or with each other. These different structures made it possible to provide fibres with different rates of absorption, with different degrees of stiffness or flexibility, and for use in monofilaments, braided multifilaments, and other yarn structures, as required for different surgical operations.

9 POLYCARBONATES

Polycarbonates form a rather specialised class of linear polyesters, since they are formed from a diol, usually an aromatic diol, with a derivative of carbonic acid. The commercially useful products also differ from other types of polyester in that they are generally non-crystalline, melt-processable polymers of high T_g, possessing very high optical clarity and toughness.

One of the earliest reports of a reaction that can now be interpreted as forming a polycarbonate came from Birnbaum and Lurie in 1881 [88]. They reacted resorcinol, phosgene and pyridine, but assigned a cyclic carbonate structure to the product. In 1898, Einhorn [89] repeated this work and also used hydroquinone and catechol. He assigned a polymeric structure to the products from hydroquinone and resorcinol, and a cyclic structure to the product from catechol. Bischoff and van Hedenström [90] confirmed this work by using ester exchange with diphenyl carbonate (DPC) as the synthetic method. Thus, the two main synthetic methods were both used at an early stage. In 1930, Carothers published the results of his syntheses of polycarbonates, mainly from aliphatic diols but including *p*-xylylene glycol, and diethyl carbonate, both directly and through intermediate cyclic carbonates. Most of the polymers were crystalline but of too low a melting point to be useful in their own right, although a poly(*p*-xylylene carbonate) melting at about 180 °C was isolated but not examined further [91].

Much the most important polycarbonate in commercial terms is made from 2,2-di(4-hydroxyphenyl)propane, commonly known as bisphenol A. This polymer was discovered and developed by Farbenfabriken Bayer [92]. The synthesis and properties of this and many other polycarbonates were described by Schnell in 1956 [93]. The polymer became available in Germany in 1959, and was given the trade name *Makrolon* by Bayer (in the USA, *Merlon* from Mobay). General Electric (GE) independently developed a melt polymerisation route based on transesterification of a bisphenol with DPC [94]. Their product, *Lexan*, entered the US market in 1960. The solution polymerisation route using phosgene has since been displaced by an interfacial polymerisation.

10 NATURAL POLYESTERS

10.1 OCCURRENCE

Polyesters are found in nature in a wide range of bacteria and also in higher plants. In the case of bacteria, two types of polymer have been identified [95]. One type consists of poly(3-hydroxybutyrate) (PHB), also known as poly(β-hydroxybutyrate), and its copolymers with related repeating units, particularly 3-hydroxyvalerate. These polymers are produced within the bacteria and stored in an inter-cellular granular form for consumption in times of hardship. The other type consists of poly(β-malate) (poly(L-3-carboxy-3-hydroxypropionate)), which has the same carbon skeleton as PHB but which does not appear to be used as a storage reserve. In the case of higher plants, again two types have been identified [96], with both having complex network structures. *Cutin* plays a structural and protective role at the surfaces of plants. It is based mainly upon C_{16} and C_{18} fatty acids that have various degrees of substitution by hydroxyl groups, and in some cases also contain 9,10-epoxy groups. *Suberin* occurs in outer cell walls as a barrier against environmental stress. This material is even more complex, since its aliphatic polyester domains are attached to aromatic domains derived from units such as 3,4-dihydroxycinnamic acid.

Polyesters are also produced naturally in some animals. In particular, shellac is a natural product that was for many years of major commercial importance as a moulding resin (e.g. for phonograph records) and a varnish. It is a constituent of lac, which is secreted by the lac insect of S. E. Asia and exuded by it onto trees. Shellac, which is obtained by purification from lac, is a complex polyester which can be hydrolysed to polyhydroxylic acids such as 9,10,16-trihydroxyhexadecanoic acid [97].

10.2 POLY(β-HYDROXYALKANOATE)S

In 1925, Lemoigne [98] described the isolation of an aliphatic polyester, poly(β-hydroxybutyrate) (PHB), from the cytoplasm of the bacterium *Alcaligenes eutrophus*. This polymer is synthesised by the bacterium for storage as a reserve against times of famine, and can be consumed enzymatically with release of energy whenever such times occur. The proportion of the mass of the bacteria attributable to this polyester can be very high, well over 90 %. Numerous bacterial species of different types, Gram-positive and Gram-negative, aerobic and photosynthetic, have since been shown to synthesise this polymer. The feedstock for the synthesis is normally of carbohydrate origin, for example, glucose, but the bacteria can be induced to transform other organic chemicals, such as

methanol, into the polymer. Lemoigne found that chloroform was the best solvent for extracting the polymer from the bacteria of those he tried. About 20 % (by weight) of the dried bacteria consisted of this material, which he found melted at 157 °C. He concluded that the extracted material was a product of dehydration and polymerisation of β-oxybutyric acid, with the empirical formula $(C_4H_6O_2)_n$. He referred to this as a polylactide, although by modern terminology this would not be correct.

During the period 1960–1962, W. R. Grace and Company filed several patents that claimed methods of extracting poly(β-hydroxybutyric acid) from bacteria and its use for making absorbable prosthetic devices, particularly sutures [99]. The polymer was said to be degraded by esterases in the body. This degradation was too slow to be competitive with existing degradable sutures, so no commercial product appeared.

In the 1970s, ICI introduced this polymer and copolymers in which it was the major constituent as commercial products, initially under the acronym PHB, and a little later under the trade name *Biopol*, which referred specifically to copolymers containing β-oxybutyrate and up to 30 % of β-oxyvalerate repeating units. The copolymer is more flexible and tougher than the homopolymer [100, 101].

11 CONCLUSION

The foregoing summary of the history of polyesters to date illustrates the diversity of chemical structures available and the wide range of uses to which they have been put, although it is far from being exhaustive. There can be no doubt that polyesters will continue to be one of the most important classes of polymer. Predictably, as the supply of cheap fossil-fuel-based chemical primaries declines, biological sources can be persuaded to yield appropriate intermediates and even polyesters themselves.

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