

Chapter 5

Polymeric Materials for Rapid Manufacturing

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5.1 Introduction

Rapid Manufacturing also known as solid free-form fabrication is a term describing a range of processes whereby a computer generated design is converted to a three-dimensional (3D) object. This methodology was originally used for the manufacture of models and prototypes (hence the description “Rapid Prototyping”) [1] and has becoming an increasingly important tool for designers and manufacturers [2]; indeed in some cases this approach is being extended to the manufacture of small numbers of complex articles. One particularly exciting development is the use of Rapid Manufacturing for the production of biocompatible components for medical use, where the production of a one-off component is a necessary requirement. Examples include the manufacture of dental prostheses [3] and hip joints [4].

Perhaps the best known of this group of rapid manufacturing techniques is Stereolithography. Here, a polymer (usually highly cross-linked) is formed layer by layer *via* photoinduced polymerization; the light source, which is either a highly focused beam or a laser, is used to initiate polymerization through the photodegradation of an initiator to form radicals, cations, or carbene-like species as discussed below. This maximizes dimensional control, with ultimately the resolution being determined largely by the wavelength of the excitation light (see below). A related approach is that of selective laser sintering; in this case, a layer of powder is laid onto a surface and a CO₂ (or similar) laser sinters, i.e. heats and fuses together, the powder. Such systems can be utilized to form objects from polymers, ceramics, and metals [5]. A rather different approach is to deposit the material (also one layer at a time) through a nozzle; this approach includes techniques where conventional/ink-jet printing processes, are converted to 3D systems (once again in a layer-by-layer approach) or systems where a fine-stream of polymer is pushed out on to the surface, a technique known as fused deposition molding [6].

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Of the many types of materials which may be used, the most common include metals [7], ceramics [8], and polymers [9]. Each of these materials may offer different advantages in terms of factors such as mechanical strength and biocompatibility, but in the case of polymeric systems it is their versatility which makes them particularly attractive; and it is these materials which form the basis of the discussion included in this chapter. In all the typical rapid manufacturing system, the computer converts the design into layers and then the solid object is prepared layer-by-layer; it is intended in this discussion to outline the types of materials available for manufacturing by this approach, their advantages and limitations, and in particular to compare how the properties of articles manufactured in this way differ from those prepared by conventional approaches to polymer manufacturing, such as molding extrusion, and casting.

5.2 Polymeric Materials

5.2.1 Polymerization

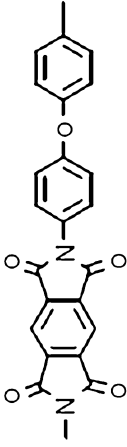
In principle, the synthetic chemist can produce an almost infinite variety of organic polymers, by virtue of the versatility and controllability of organic chemistry. The reality is somewhat more restrictive. Commercial enterprises are constrained to those materials manufactured industrially, and cost is a frequent restriction (though this will depend on the application). Thus, commercially, some polymers are classified as commodity plastics; these are cheap to produce in a high volume but their physical properties will be unremarkable (Table 5.1).¹ In contrast Engineering Plastics tend to be more expensive largely because they are produced in lower quantities, but also because they have specific superior properties, examples of which include mechanical strength or thermal stability. Polymers are also classified according to their processibility and may be referred to as thermosetting or thermoplastics; the former are materials which once processed cannot be melted or dissolved to form new objects, this is usually due to extensive cross-linking.² Thermoplastics can be melted or solvent processed, a factor which is important in their manufacture and in recycling. The majority of commodity and engineering plastics tend to be thermoplastics [10].

Historically chemists tended to classify synthetic polymers as addition polymers or condensation polymers. The original definition of Carothers [11] required, that for addition polymers, the molecular formula of the monomer should be identical with the structural unit, while for condensation polymers the monomer should

¹ That being said the strength to weight ratio of polyethylene which allows the production of huge (and problematic) numbers of polyethene bags, can hardly be said to be unremarkable, other than in terms of the ubiquitous nature of these articles.

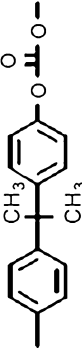
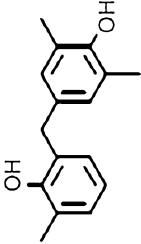
² This definition also might apply to rubbers, but rubbers are deformable; thermosetting plastics are generally rigid.

Table 5.1 Some typical polymers, classifications, and uses

Polymer	Repeat unit	Commodity polymer	Engineering polymer	Step growth	Chain growth	Comments
Polyethylene (Low-density)	$-\text{CH}_2\text{CH}_2-$	✓		✓	✓	Produced in high volume many uses in for example packaging.
Polyethylene (High-density)	$-\text{CH}_2\text{CH}_2-$	✓		✓	✓	Non branched produced by Ziegler Natta process used for bottles, pipe, cable insulation.
Polypropylene	$-\text{CH}_2\text{CH}(\text{CH}_3)-$	✓		✓	✓	Rope, cordage, car parts, containers.
Poly (vinyl chloride)	$-\text{CH}_2\text{CHCl}-$	✓		✓	✓	Pipes flooring, wire insulation building materials.
Polystyrene	$-\text{CH}_2\text{CHPh}-$	✓		✓	✓	Packaging (foam and films) insulation.
Polyethylene Terephthalate	$-\text{OCH}_2\text{CH}_2-\text{O}-(\text{C}_6\text{H}_4)-$	✓	✓	✓	✓	Unusually considered both as a commodity polymer and an engineering polymer. Used to make soft drink bottles and fibers (especially fleeces).
Polyamide	e.g. $-\text{CONH}(\text{CH}_2)_5-$		✓	✓		Polyamides are used to form fabrics orientation in fiber formations
Polyimide			✓	✓		The example shown is Du Ponts Kapton. Resistant to high temperatures used e.g. to insulate wires.

(continued)

Table 5.1 (continued)

Polymer	Repeat unit	Commodity polymer	Engineering polymer	Step growth	Chain growth	Comments
Polycarbonate		✓	✓	✓		High impact strength- used for safety shields safety helmets etc.
Phenol formaldehyde resin				✓		Highly cross-linked system thermosetting polymers. Thermosetting-Plastic
Rubber	$-\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2-$					Natural polymer – lightly cross-linked to form an elastomer.

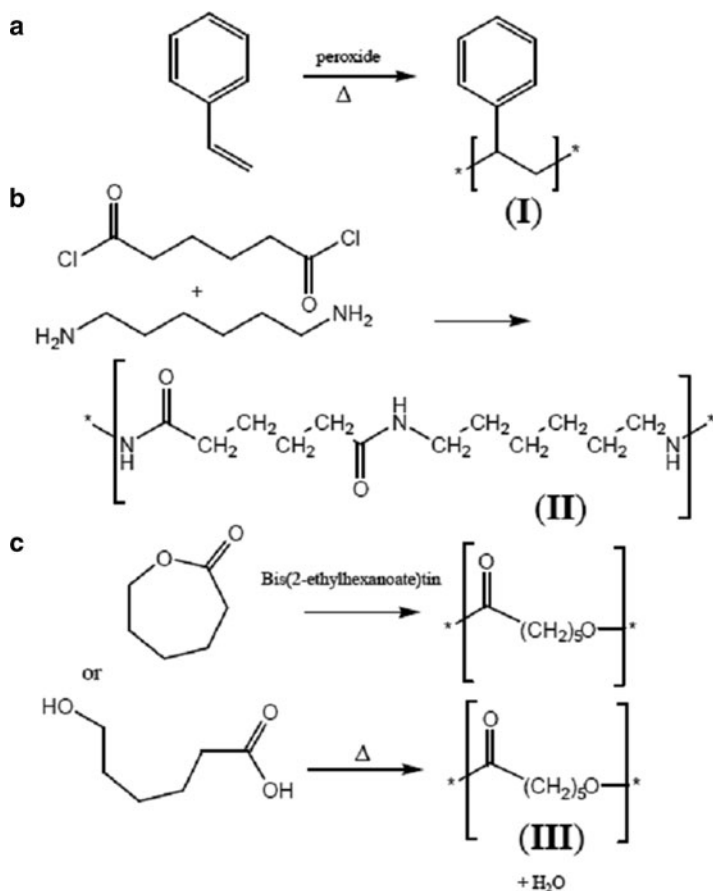


Fig. 5.1 (a) Polymerization of styrene via a chain-growth process, (b) formation of Nylon 6,6 via a step-growth process, and (c) alternative chain-growth (*top*) and step-growth (*bottom*) routes to poly(ϵ -caprolactone)

be different, with the polymer obtained from the monomer by intermolecular condensation. On this basis polystyrene represents a simple addition polymer (Fig. 5.1a), while Nylon 6,6 produced from adipoyl chloride and hexanediamine (Fig. 5.1b) is a typical condensation polymer. However, although these terms remain in usage, they can give rise to confusion, particularly in cases, where a similar polymer can be produced from either mechanism (as in the case of the polyester shown in Fig. 5.1c). As a consequence, polymer chemists tend to classify polymers according to the way in which propagation occurs. Where propagation occurs in a stepwise fashion we have a step-reaction or step-growth system. Where there is addition of a monomer unit onto an activated polymer chain we have a chain-reaction or chain-growth polymer. The importance of this in relation to the usage of polymeric systems in rapid processing applications will become clear from the following discussion.

For chain-growth systems polymerization requires initiation by an activated species such as an anion, a cation, and probably most commonly, a free radical [10]. The initiated chain can react with many monomers to form material of quite high molecular weight. In this case all initiated chains are converted to high molecular weight polymer, quite early in the reaction and consequently the polymerization mixture consists of high polymer and monomer. This requirement for initiator means that chain growth systems are in most cases the systems of choice when photoinitiated polymerization is required. Because of the nature of the polymerization process, step-growth polymers are less readily formed photochemically; thus no initiator is required for step-growth system. This further differs from the chain growth in that all the monomer is partially reacted quite early in the process. However, high molecular-weight polymers are difficult to obtain, and only occur at high conversion; fortunately such systems are often produced from functionality which leaves groups with dipoles, or the potential to form hydrogen bonds in the final polymers. The consequence of this is that notwithstanding the difficulty in producing high molecular weight materials, intermolecular forces are often higher in engineering polymers than commodity polymers. Thus such systems may be the ideal material for applications where high mechanical strength is required, but may not be so readily produced in situ as part of the prototyping process.

While the synthetic origin of a polymer is important the way in which a polymer is processed, it is also a major factor in determining the properties of the materials. A full discussion of the possibilities is beyond the scope of this article, but it is important to note that processing, in particular, techniques such as extrusion or spinning impart additional mechanical strength to the polymer system through promoting backbone crystallization and alignment. This is particularly the case for step-growth systems; it is spinning for example which imparts the high strength to polyamide fibers such as Nylon 6 and Kevlar; indeed with careful processing polyethylene can be made to be as strong as these latter materials [12].

5.2.2 *Cross-Linking*

One significant property of polymers not present in low molecular weight compounds is the possibility of forming cross-links between neighboring chains. This cross-linking means that the chains have restricted translational mobility. From the point of view of the applications described here, this cross-linking provides 3D stability; additionally such materials cannot melt (for crystalline polymers) or dissolve. This last point is particularly important in the development of 3D prototypes since it can ensure that the final material can be separated from monomer or prepolymer. Cross-links may be formed post-polymerization by the presence of reactive units in the chain of a polymer,³ as is the case for the vulcanisation of natural rubber (utilizing the reactivity of carbon-carbon double bonds in the polymer backbone) and it is this approach which is used in many stereolithographic techniques. Alternatively, cross-linked systems may be formed during polymerization if the functionality of the monomer is greater than

³ It is important to form such systems that the side-groups exhibit different reactivity to the polymerisable units in the monomer prior to polymerization.

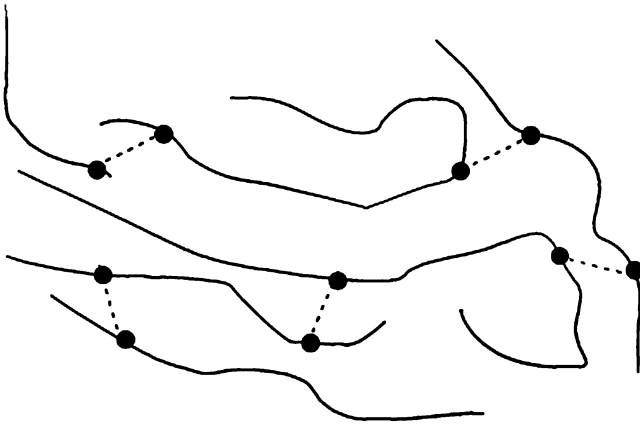


Fig. 5.2 Schematic representation of cross-linking in a polymer (the broken line represents short-length cross-linking chains)

required for a linear polymer (an example of such a case is the phenol formaldehyde resin shown in Table 5.1).⁴ Here the final form of the polymer must be determined prior to polymerization; an illustration of such a system is the use of polyurethanes in reaction injection molding [15]. The properties of the cross-link system have a high dependence on the density of cross-links, for example with low cross-link density then rubber elasticity is possible, with the polymer showing reversible deformation; higher cross-link densities give rise to extremely intractable hard resinous materials.

The production of 3D polymeric materials can be achieved in many ways, but a particularly common one is *via* photochemical polymerization or cross-linking. The use of optics, and particularly lasers provides a high level of spatial control and resolution; this can be couple directly to a computer design. The following section details ways in which visible and ultraviolet light can be used to initiate polymerization or crosslinking and describes the properties obtained from various material combinations (Fig. 5.2).

5.3 Photopolymerization

5.3.1 Free-Radical Systems

Although photopolymerization can be induced in a number of ways, the most commonly used systems involve the mediation of free radicals. The interaction of

⁴ It is also possible that photoactive units can be added which degrade the polymer chain to form for example free-radicals, which may themselves combine [13, 14]; similarly ionising radiation (e.g. γ -radiation) will induce free-radical formation on the chain; the high energies involved may result in unwanted degradation products such as chain-scission.

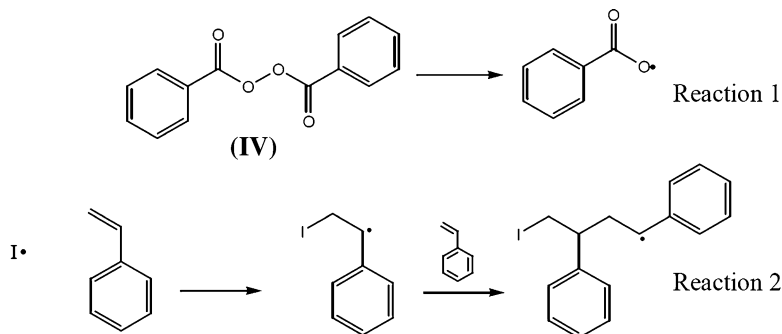


Fig. 5.3 Photolysis of benzoyl peroxide produces predominantly benzoyl radicals; these can add to a vinyl monomer such as styrene to produce a polymeric species

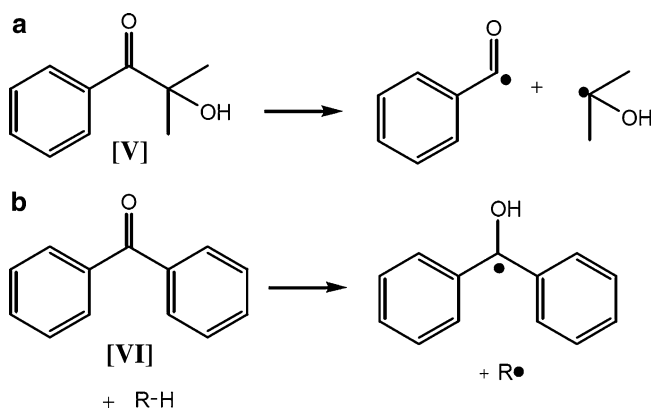


Fig. 5.4 Type I (a) and type II (b) photodegradation of aromatic ketones; the radicals produced can initiate polymerization

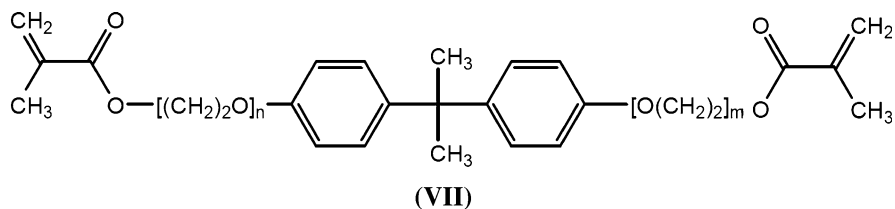
light can produce free radicals via homolysis of weak bonds as in the homolysis of benzoyl peroxide (Fig. 5.3 – Reaction 1); alternatively, the generation of a triplet species from a ketone can be thought of as the formation of a di-radical. This is the case with the type II photodegradation of ketones [14, 16], as shown in Fig. 5.4.

In the Type I case cleavage occurs; Type II systems react by triplet formation followed by hydrogen atom abstraction. The radicals produced add on to vinyl systems such as styrene (Fig. 5.3 Reaction 2) to induce polymerization or to add on to reactive units in the polymer chains. Common free-radical initiators include the peroxides and aromatic ketones described above but others including the azo compound 2,2'-azobis (2-methylpropionitrile). The most common monomer systems are acrylates and methacrylates, for example the Monomer (VII) is commonly (with $m=n=1$) is often used in dental applications [17]. Styrene based resins are also used in some applications; this mono-functional monomer alone, however, will produce a polymer

Table 5.2 Factors Influencing Behavior of photopolymer systems [18, 22]

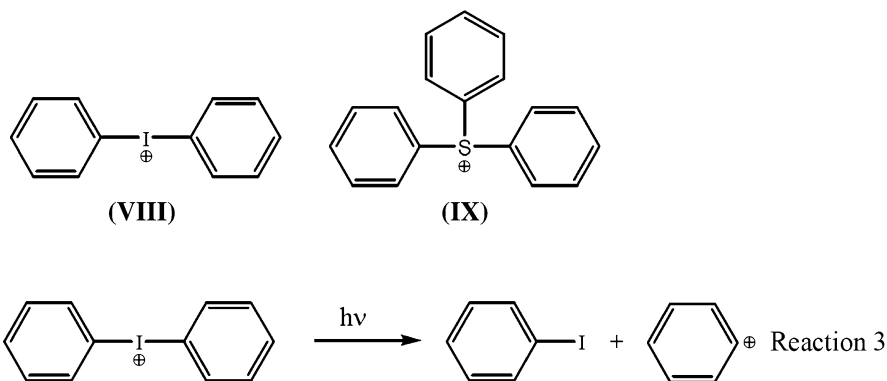
Factor	Consequence
Switch from mono to diacrylate	Rate of polymerization increases and material becomes cross-linked; flexibility decreases; hardness increases, improved solvent resistance
Switch from di- to tri-acrylate	Rate of polymerization increases and material becomes cross-linked; flexibility decreases; hardness increases, improved solvent resistance; more unreacted alkene groups
Use of styrene rather than acrylate	Lower cure speed
Changing the linking groups in a diacrylate	Aliphatic polyurethanes give soft flexible materials; aromatic polyesters and polyethers produce hard scratch resistant coatings
Use of mono-acrylate containing two oxygen atoms in a heterocyclic structure	Greatly enhanced reactivity and speed of cure
Pigmented system	Polymerization is less efficient as less light available to interior of sample – switch to specialist initiator required
Change of excitation wavelength to shorter UV	Resolution improves (130 nm for 193 nm excitation wavelength), problems with penetration deep into the sample
Use of siloxane system	Lower glass transition temperature, and more flexible final product
Cationic system	Oxygen less important; reaction may continue in dark In general cationic polymerization is slower than radical process (particularly for epoxy systems) Moisture interferes with cationic systems – not with radicals Shrinkage less of a problem for cationic systems

which is soluble in a range of common solvents. Thus it is combined with an unsaturated polyester (containing for example maleic or fumaric acids) to produce a cross-linked material. Decker [18], however, suggests that this material, while used in some applications due to the low cost of the monomers, is generally inferior to acrylate systems in terms of cure speed and subsequent material properties. The structural advantage of acrylates and methacrylates is demonstrated by (VII); the acid functionality of the basic unit allows for an almost infinite structural variation, including the incorporation of both flexible and rigid units, and by having diacrylates (or even triacrylates) ensuring that photopolymerization is accompanied by cross-linking. The consequences of such modifications are indicated in Table 5.2.



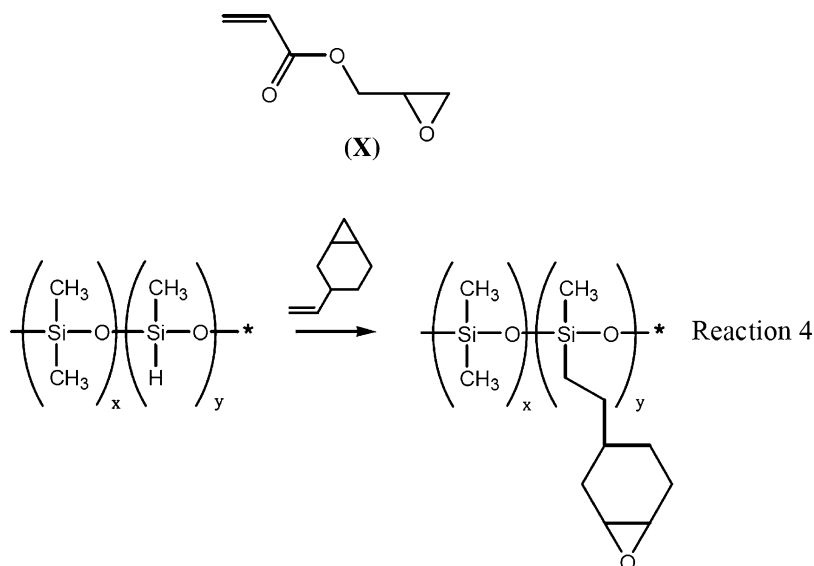
5.3.2 Cationic Systems

Photoinitiation of cationic chain-growth polymerization is also relatively common [19], a range of systems are used but commonly these involve triarylsulfonium (IX) and diaryliodonium (VIII) salts. Photolysis of these compounds results in the formation of aryl cations [Reaction 3], although other species such as cation radicals and radicals may be formed by a competing homolytic process.⁵ The cation species may themselves initiate polymerization or they may generate Brönsted acids by subsequent reactions which then react with the monomer. There are a range of monomers which may be polymerized by these initiators (indeed any monomer which can be polymerized cationically might be expected to react); however those most commonly found in the type of application of interest here are vinyl ethers and epoxides. The system is to some extent complimentary to the free-radical systems, these monomers are not generally polymerized by such means. Furthermore, cationic polymerization can proceed in the presence of oxygen and (once ionic species have been produced) the polymerization can occur in the absence of light; the polymerization may be to some extent living. In marked contrast, free-radical polymerizations will discontinue within a fraction of a second on removal of the light source.

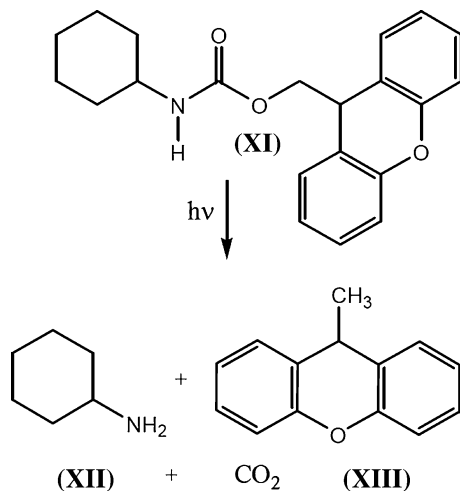


A particular advantage of cation systems especially epoxides is that they offer the potential of postpolymerization cross-linking; thus they may for example be incorporated as side groups on a vinyl monomer without involvement in the free-radical process, vinyl ethers in contrast, although poorly reacting in many circumstances, may become involved in the free radical process [20]; this can result in premature cross-linking which will of course prevent the shaping of the resin. The choice of epoxide is important, thus while glycidyl ether (X) is rather slow to react; cyclohexyl epoxides are cured rather more rapidly, a fact that has been used [21] to prepare photocurable polydimethylsiloxanes [Reaction 4].

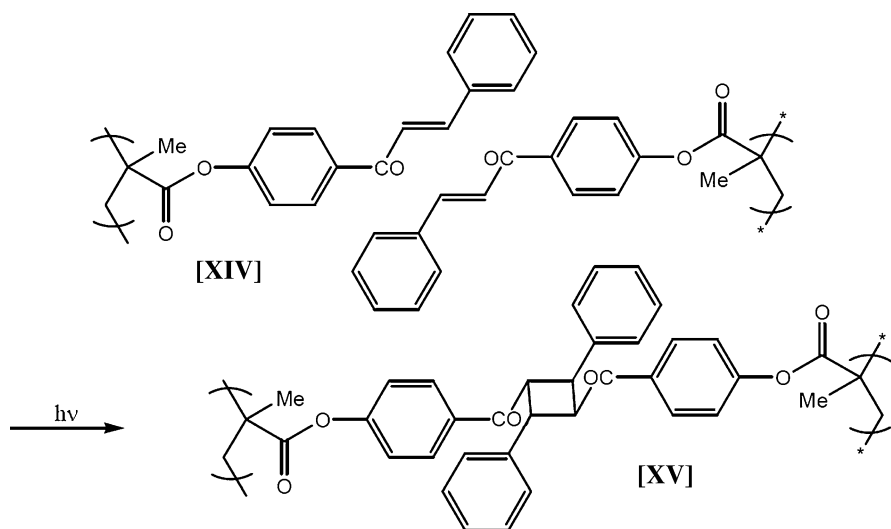
⁵ Radicals produced may themselves react with the “onium” to form cationic species and a further radical – thus giving unexpectedly high quantum yields for initiation [19].



While the use of the photogeneration of free radical species and cations (particularly acids) are common features of photopolymerization, there may be disadvantages; free-radical polymerizations for example are inhibited by oxygen. In this regard the photogeneration of bases represents an attractive alternative. There are, however, substantially fewer anionic initiated photopolymerization systems, although recently some promising systems are being developed [23]. An example of a photodegradable carbamate is shown (XI); in this case a primary amine (XII) is generated [24]. In general the amines produced can be used to initiate an anionic polymerization; amines such as this have often been used to cross-link epoxy systems [25]; alternatively cyclopentadienyl anions generated from metallocenes have been used to polymerize cyanoacrylates [26].



The discussion above has focused on initiators for chain growth processes; however there are some photoreactions which do not involve the generation of a reactive initiator. Perhaps the best known of these reactions is the $2\pi + 2\pi$ photocycloaddition of alkenes; in principle this could be used to produce a polymerization (in a step growth manner) in practice this is often used to cross-link a preformed system by the photodimerisation of pendant side groups. In this regard α,β -unsaturated carbonyl compounds are particularly useful [27] and polymers with cinnamic acid [XIV] side groups have been successfully used as negative photoresists (see below). Photodimerisation reactions have also been used as topological polymerizations [28].



5.4 The Two-Dimensional Case Polymers for Photolithography

The development of 3D prototyping could be considered as an extension of the two-dimensional (2D) variants, particularly as a layer-by-layer approach is often used. In this section we look at one such approach namely photolithography; this shares many features with this well-known 3D process, stereolithography, and moreover this technique can be applied to the construction of solid objects itself, particularly at the nanometre level [29] and we discuss this first. Photolithography is a technique which has developed over many years; it involves coating a surface with a light sensitive material, often a polymer, and exposing selected areas to light by means of a mask. This methodology is particularly important for the manufacture of microelectronic components [29, 30], but has been seen as having great potential in other areas such as microfluidic systems [31].

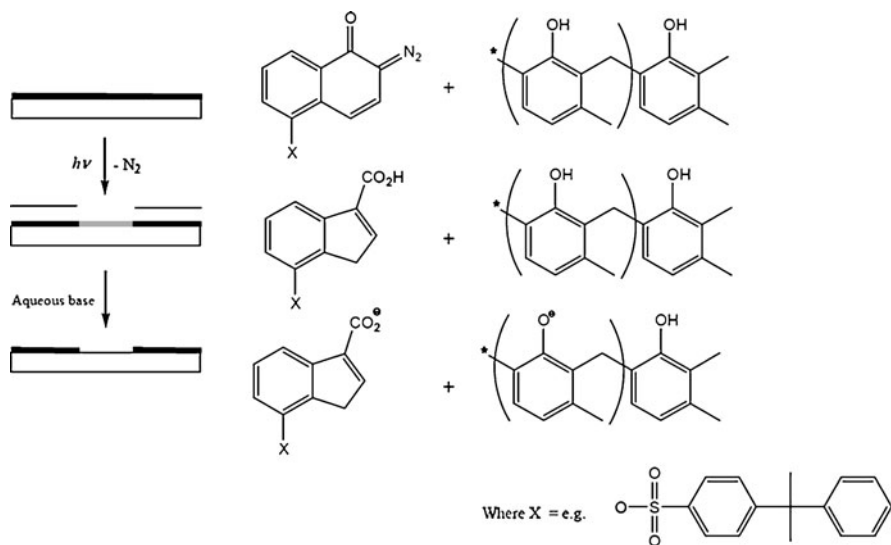
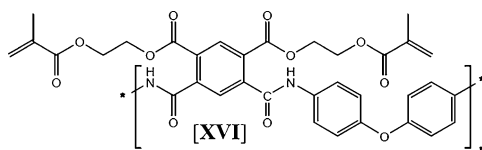


Fig. 5.5 A positive photoresist: In the presence of the ketone the polyphenolic compound is insoluble. Irradiation at the appropriate wavelength results in the formation of the acid shown and the polymer becomes soluble in aqueous base. The irradiated area can be dissolved away

Photolithography methodology is particularly important for the manufacture of microelectronic components. There are two major classifications of this technology: a positive photo resist is one where the area exposed to light becomes soluble and is removed in the process; for a negative photoresist the area exposed remains insoluble. The positive variant is exemplified by the well-known Novolac system [30]; here the presence of the anthraquinone is designed to make the polymeric phenol system insoluble. On irradiation, the photochemical transformation indicated in Fig. 5.5 results in a mixture which is soluble in basic solution; but only in the irradiated regions; thus only the irradiated portion can be removed. This system has a number of advantages including nontoxicity of the developing medium, and superior plasma etch resistance; the best systems of this type have been used to construct integrated circuits with features as small as 350 nm [32].

As stated above negative photoresist become less soluble (or indeed insoluble) in the exposed areas. This may be achieved by altering the polarity of the polymer, by changing the oxidation state within the system, or through crosslinking. The earliest systems were based on poly (vinylcinnamate) [33]; here photo cross-linking is achieved by the $2\pi + 2\pi$ photo cycloaddition of the alkene. This technology, first marketed by Kodak, was first applied to printed circuit boards, nowadays, many other systems are applied; these include Novolac systems and (meth)acrylates. While there are many materials for such applications a typical example is provided by the polyimide precursor (XVI) shown below, which is cross-linked photochemically to form an insoluble material; on removal of the unreacted precursor, heat

treatment results in the formation of a polyimide. Polyimide photoresists are particularly attractive because of their high thermal stability [34], but other multifunctional acrylics can be used.



The systems described above are entirely satisfactory for the production of printed circuits; however, there are problems with resolution; it would seem that the resolution provided by these systems is poor [30, 35] thus while suitable for the manufacture of printed circuit boards, the requirements for resolution for the microelectronics industry are more stringent and other systems are favored.

A commonly-used negative photoresist [36] is the cyclized polyisoprene system (XVIII) [30], which is used in the microelectronics industry when high resolution is not required. Here cross-linking is provided by a bisazide which on irradiation produces nitrene units (analogous to a carbene); these insert in the double bonds in the isoprene system leading to a cross-linked structure, as illustrated in Fig. 5.6; such resists are imaged with wavelengths above 436 nm [30]. In fact it may not be necessary to introduce extensive cross-linking into the system since a small proportion of linked chains may render the polymer sufficiently insoluble [28], except that lightly cross-linked systems may swell in the solvent used to remove unreacted material consequently; this may adversely affect the film boundaries. An alternative popular resist material is SU-8, which is an epoxy based system [11]. Here the polymer (based on the Bisphenol A system) is cross-linked on irradiation by a photocationic initiator as described above. A particular feature of this is that the

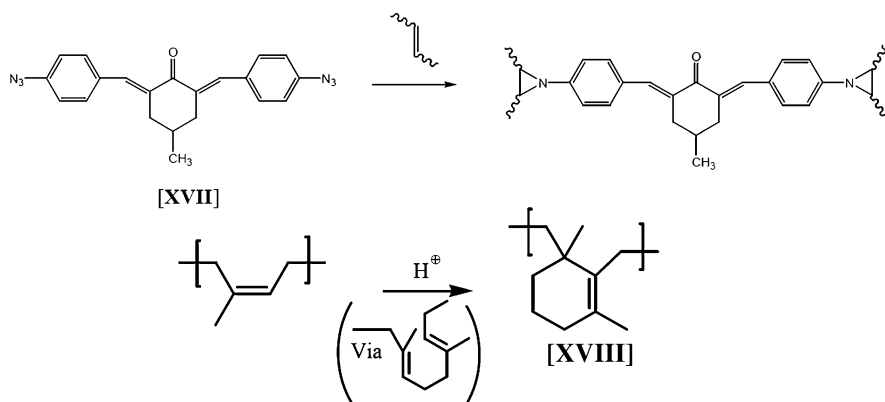


Fig. 5.6 Bisazide [30] used in photo-crosslinking carbon-carbon double bonds in a polymer backbone

material has a relatively low absorbance at the irradiation wavelength (typically 365 nm), which means that light can penetrate significantly through the sample. Thus this is the material of choice for high aspect ratio materials [37] and coatings of up to 3 mm may be prepared. The ability to prepare micron- scale-structures with substantial depth has considerable potential in the area of microelectromechanical systems [38]; in such applications the methodology is no longer 2D, but the size of these objects are rather smaller than that we are considering in this chapter.

5.5 The Three-Dimensional Case Polymers for Stereolithography

The potential of resists systems is enormous and based on well established principles; however, with the exception of high aspect ratio photoresists, the technology is largely concerned with 2D imaging. For 3D imaging alternative methodologies are used; however, possibly the most commonly used methodology essentially adopts photochemical development of a surface film of polymer and adapts it to three dimensions; this process is known as stereolithography. Here a solid prototype is constructed via the computer control of a laser, which writes onto a liquid polymer precursor to solidify the material. The process simply writes a particular structure on layer after layer of the polymer until the solid object is produced. Thus, most of the chemistry involved bears close similarities to that used for negative photoresists; in particular the use of cross-linking to solidify an object. Previously the method was found to be expensive and time-consuming, so its use until recent years has been restricted mainly to the construction of prototypes. More recently the method has been developed and commercialized by companies such as 3D Systems of Valencia California and machines such as that shown in Fig. 5.7 are now available [39].

The development of commercialized Stereolithography systems has been accompanied by rapid improvements of the resins available. That being said, most resins rely on the radical polymerization of (meth)acrylates or cationic polymerization of epoxides (or vinyl ethers) and in fact might be formulations containing both. The fundamentals of this chemistry has been discussed above in Sections 5.3 and 5.4; thus compound **VII** used in dental applications may also be used in stereolithography; however, other resins may be based on acrylate-terminated systems for example, polyurethanes, polyesters, polyethers and polysiloxanes, acrylate capped butadienes and acrylamide related systems have also been used. Diacrylates provide cross-linked systems, but more rapid hardening is provided by the use of triacrylates; mono-functionalised acrylates are often put in to reduce the viscosity of the pre-polymer system; it will modify the cure extent and can usefully help to control the properties of the final polymer [40]. Clearly there is substantial scope for modifications, for example the polyurethane system [XXII] shown in Fig. 5.8 is one of a range of similar materials which could be selected. Aliphatic or aromatic diisocyanate might be incorporated; in the example shown the

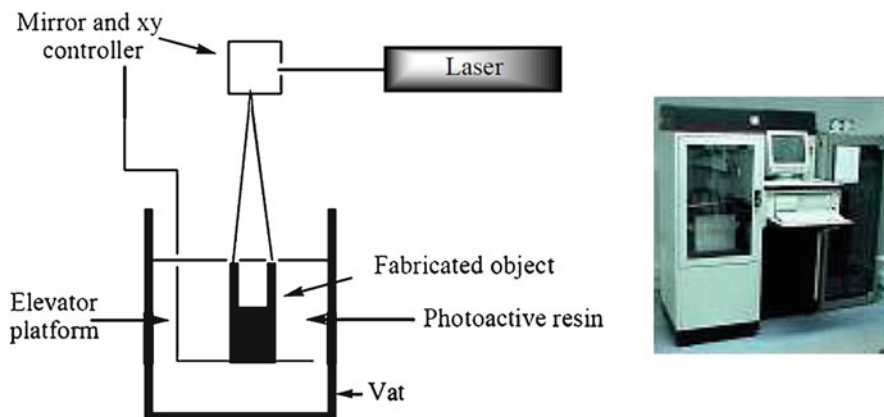


Fig. 5.7 Schematic of the stereolithography process and picture of an actual instrument (by permission of 3D systems Valencena California)

aromatic isocyanate will increase the hardness over that which might be found were an aliphatic isocyanate such as hexyl diisocyanate used. The properties will also depend on the molecular weight of the poly(propylene glycol) used, and for a more rigid system a polyester can replace the central polymer. Similarly, for the polyester based systems (e.g. [XXI]) the nature of the polyester can have a dramatic effect on the reactivity of the resin and also alter the hardness, stability, and the aging properties of the polymer; typically higher molecular weight diacrylates are more viscous, but less reactive and give a more flexible material than the lower molecular weight analogs. There is some interest in the use of liquid crystalline materials in such systems as a way of introducing anisotropic orientation and additional strength [41].

As with the acrylic system there is potentially a diverse range of vinyl ethers and epoxides systems such as those shown in Fig. 5.8, which can be polymerized by a cationic mechanism. Many complex vinyl ethers have been made in laboratory studies, but the industrial application have been to some extent restricted due possibly to the difficulties associated with preparing these monomers particularly as they are usually produced via addition to acetylene [19].⁶ Though in fact rather less reactive than vinyl ethers, the epoxides, however are generally more accessible synthetically, but the wide range of monomers available have not been exploited in the same way as for the acrylic systems above. Interestingly, cyclohexyl systems such as [XXVI] are often preferred; this is because the cyclohexyl systems are particularly rapidly photopolymerized (a result of additional strain on

⁶ Vinyl alcohol is of course the thermodynamically unfavoured enol tautomer of ethanal and thus the ether is generally formed by addition of ROH across the acetylene triple bond.

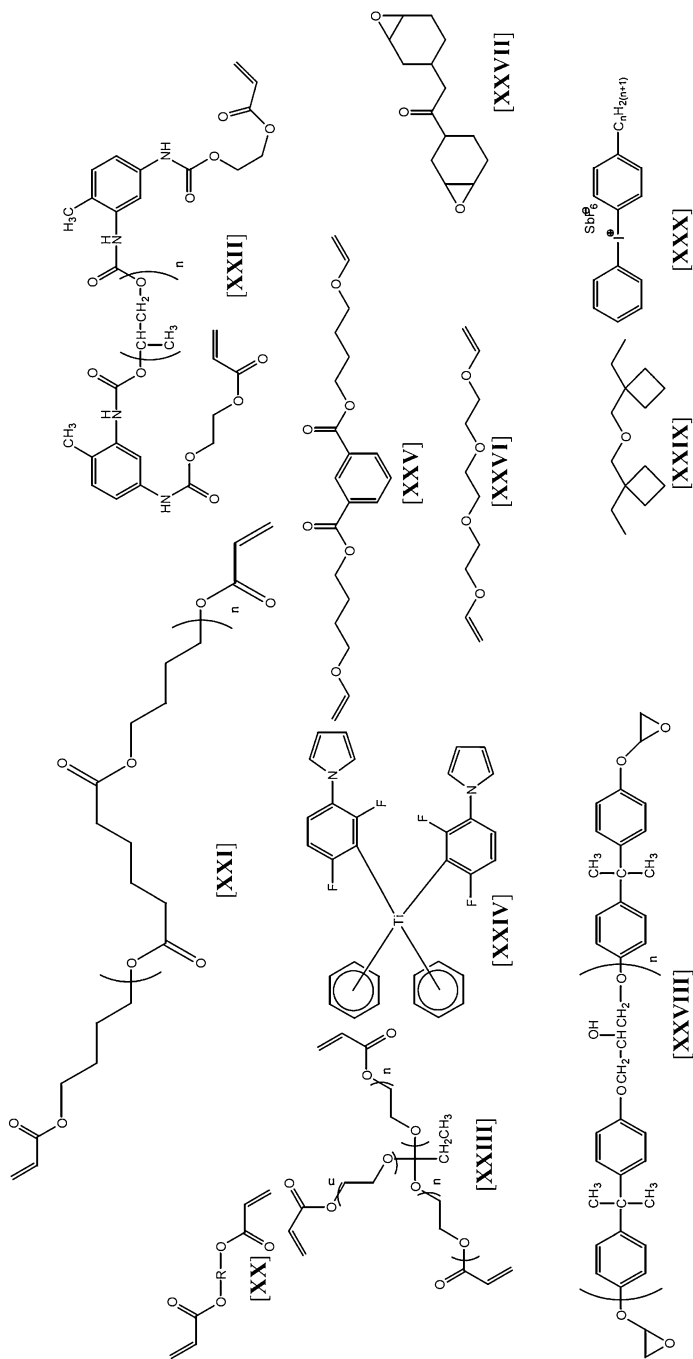


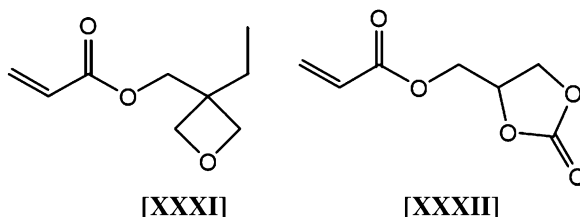
Fig. 5.8 Range of monomers and initiators used for stereolithography; acrylates (and methacrylates such as those shown in structures [XX] to [XXIII]) are initiated by free radical initiators, a particularly effective one is Irgacure 784 [XXIV], which sensitive to light with wavelengths of up to 500 nm.; vinyl ethers ([XXV] and [XXVI]), epoxy-based systems [XXVII] and [XXVIII], and the 4-member analog such as [XXIX] can be polymerized by cationic initiators, of which [XXX] is a typical example

the molecule); glycidyl ethers such as [XXVIII] polymerize rather slowly, and it would seem that the polymerization is subject to an induction period arising apparently from an activation energy barrier to propagation; this can be overcome thermally (and may give rise to some interesting spatial aspects to the eventual polymerization), but not suited to the time scale of the stereolithographic process [42]. Although a range of initiators can be used the iodonium system [XXIX] is often preferred; the alkyl chain being tailored to modify the solubility of the initiator and the hexafluoroantimonate anion is chosen by virtue of its extraordinarily weak basicity [21]. In an analogous fashion oxetane systems based on the strained four-membered oxygen containing cyclic compound are also photopolymerisable. As with the glycidyl system there is an induction period before polymerization occurs, which is less than ideal for the purpose of stereolithography; however, it has been found that the reaction can be speeded up in a number of ways; for example, copolymerising with more reactive epoxides comonomers [43] and there are some aspects of oxatanes which may be attractive in stereolithography resins (see below).

In principle stereolithography is a more precise technique than the selective laser sintering and fused deposition molding technique described below. The method should provide for precision similar to that observed with the two dimensional systems or particularly the impressive 3D structures made from high aspect ratio photoresists. In many ways, however, it is not the polymerization which limits the precision of the technology, but what happens after the light induced polymerization. In most cases post curing is needed to solidify unreacted or partially reacted monomers; this process will for example improve the mechanical properties of the prototype. The step is carried by further treating the model with UV light and heat. Unfortunately, it is often found that the additional polymerization, presumably with increased cross-linking, and the associated thermal effects results in a substantial degree of shrinkage, or warping [44]. It is the control and reduction of this problem that has driven the design of new materials. In this regard the acrylates seem to be rather more prone to problems; in particular shrinkage is substantially more for these systems than for epoxides; the shrinkage arises from a range of effects following the curing process, but it is notable that there may be some trapped radicals remaining in the acrylate samples [45]; furthermore, while acrylates and particularly multi-functional acrylates polymerize extremely quickly under the photolysis the material hardens rapidly leaving a large proportion of the polymerisable groups unreacted. The problems may be controlled to a certain extent by processing conditions, but it would still seem that epoxides provide less shrinkage, even though the polymerization may not be so rapid.

The prevention of shrinkage and the improvement of the mechanical properties of models built by stereolithography have driven a considerable amount of development into resin formulations. In fact some commercial resins appear to be a mixture of epoxides and acrylates and there may be substantial advantages in combining the two types. In addition to this it has been found that for radical systems the inclusion of monomeric acrylates improves the extent of conversion; acrylate esters of oxygen-containing cyclic systems such as [XXXI] and [XXXII]

work particularly well in this regard as rather unusually they react rather rapidly [18]. These monomers also enhance the mechanical properties of the prototype; a particular problem with the multi-functional acrylates is that they are brittle; the introduction of these comonomers results in materials with improved flexibility making them more resistant to scratching and shocks. That being said, it would seem that epoxides have the edge in the marketplace [46] and the development of such resins has succeeded to the extent that materials such as DSM SOMOS® ProtoGen™ 18120 (said to be based on oxetane chemistry) may have properties comparable to thermoplastics such as ABS.



It is probably fair to say that stereolithography represents the most advanced of the rapid prototyping methods; a natural consequence of the improvement in resin technology is that stereolithography is now being considered much more as a potential tool for the manufacture of parts, particularly when only small numbers are required. While the account above describes attempts to improve the physical properties of the resultant product through the chemical design of the polymers, other approaches have been adopted. The production of ceramic parts is particularly attractive and the use of silica filled resins has been explored in this regard [6, 46]. Problems in light scattering with high loadings of silica can apparently be avoided by the use of nanoparticles; and further improved by refractive index matching which also improves the loadings possible by minimizing Van der Waals interactions [47], although the viscosity of the resulting liquid prepolymer is problematic and requires substantial tailoring of the system. The polymer matrix may be retained, but in some cases it is removed by postmanufacture treatments resulting in a ceramic part [46]. A similar approach that has been explored is the introduction of reinforcing fibers into the photopolymer; this also imparts further strength to the final part, although the process does not seem to readily lend itself to automation [48]. Other attempts have moved away from the layering approach and used parts produced by stereolithography as masters from which silicone molds are produced. These silicone molds can then be used to produce a small number (typically 20 or so) polyurethane materials by vacuum casting, provided relatively low temperatures are used [49]; an alternative, but probably less popular option is to produce the mold itself using stereolithography [50]. That being said despite the accuracy and speed of this process, the polymeric materials may not be ideal and other related methods may be used with alternative materials, in particular, selective laser sintering and fused deposition molding may be used to produce materials from thermoplastics (indeed that the materials will melt is a requirement) and these may offer scope for further applications. Some of the materials used in these applications are discussed below.

5.6 Selective Laser Sintering

Selective laser sintering is a technique which is finding increasing importance as an alternative to stereolithography; the technique can be used for a range of polymers including nylon, polycarbonate ABS, and polystyrene. In addition, there are a range of techniques that involve polymer coated materials. This is a commercial process and involves the selective sintering layer-by-layer of a fine powder; the process is illustrated schematically in Fig. 5.9. The powder (typically 10s of microns in diameter) is spread to form a surface thickness of 75–250 μm . A laser (typically a CO_2 laser) is scanned across the surface at scanning rates between 2 and 100 cm s^{-1} . The laser is controlled by a computer design; where the design indicates the model should be solid, power is applied to the laser and the heat from the laser will fuse the region below the beam together and to the layer below. A useful consequence of this methodology is that the solid produced are supported by the surrounding powder, which eliminates the need to produce supports for overhanging parts [51].⁷ The method clearly relies on the presence of material which can be melted, so is not applicable to thermosetting polymers.

The technique of SLS can be applied to both amorphous and semi-crystalline polymers. Examples of polymeric materials include polycarbonate, polyamides, polystyrene and styrene acrylic copolymers. In terms of quality of final product, this depends on a number of factors, for example, studies of polycarbonate have shown that the mechanical properties of the final material depend on the power of the laser – if only weakly sintered then the joins between the particles form places for cracks; at

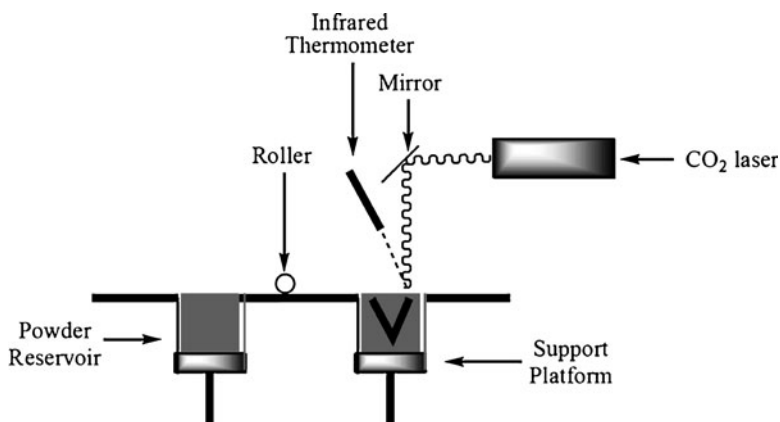


Fig. 5.9 Schematic of the selective laser sintering process

⁷For stereolithography, where the component has overhanging parts the support linking this to the main structure is not formed until after the part; this can only be solved by incorporating additional support struts into the design which are removed when the final model is made.

very high energy densities decomposition may occur [52]; in addition, of course, the heat must not be sufficient to completely melt the polymer, thus for amorphous materials such as polystyrene there is a range of sintering temperatures ranging from a few degrees below T_g to T_g ; above T_g the particles all coalesce [53]. The mechanical properties are also determined by the build orientation as there is a tendency for the fracture to occur along the directions of the layers [54]. The selection of materials is important for making molds for techniques such as investment casting, thus for example, high impact polystyrene (polystyrene strengthened by combination with butadiene rubber) is preferable to polystyrene if complex parts are to be made [53].

In addition to polymeric material there is much interest in polymer coated materials; for example a calcium phosphate ceramic material, can be made by coating particles of the inorganic solid with a polymer such as methacrylate. The polymer coated particles are then subjected to the SLS process to produce a prototype which is filled with a solution of calcium phosphate which is then dried to constant weight, and fired to yield porous calcium phosphate, as this process burns off the polymer [55]. In a similar way polymer coated metal powders offer a real approach to the rapid manufacture of metal parts [41].

5.7 Fused Deposition Modeling

The fused deposition modeling process is relatively simple as outlined in Fig. 5.10. In this system the polymer is pushed through a nozzle onto a surface, the polymer solidifies on contact with the surface and in this way a structure is built up layer by layer. The extruder nozzle is controlled by a computer program which guides where material is deposited. The material is molten as it leaves the nozzle and solidifies as it hits the surface. The layer below has to be maintained at a temperature just below the softening point of the polymer to obtain good cohesion. The technique is popular as it is applicable to a variety of thermoplastics. Thus for example materials include polycarbonate, poly (phenylsulphone), ABS, and biocompatible polymers such as poly(ϵ -caprolactone) (see below). The technique has also been applied to

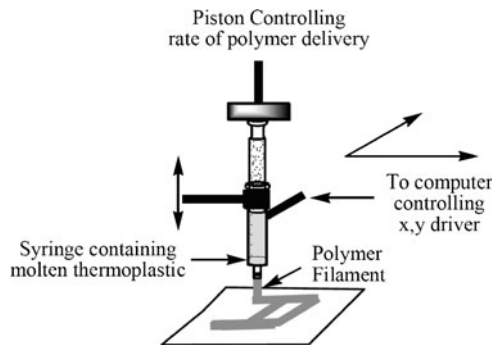
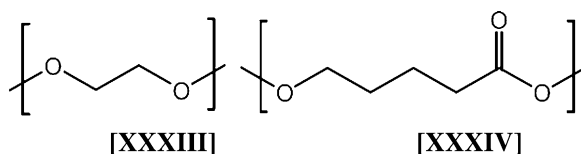


Fig. 5.10 Schematic representation of the Fused Deposition Modelling Process

the formation of a high molecular thermoplastic from a reactive monomer in a process similar to reaction injection molding; a route to forming high strength parts [56]. Polymers filled with solid particles such as iron have also been investigated and this approach is particularly promising for rapid tooling applications [57].

As discussed earlier, biological applications are an area where rapid prototyping and product manufacturing meet; thus a medical application is likely to be highly specific in both terms of size and shape as these are determined solely by the requirements of the patient. This is one area which has developed particularly rapidly over the past few years. A common problem is the development of scaffold to support tissue regeneration. The material requirements here might be quite demanding. Materials may need to be biodegradable, equally they may need to match living tissue in terms of mechanical properties; for example where scaffolds are required to support bone growth, mechanical strength, in particular compressive strength, in contrast for skin replacements may require substantial elasticity. Probably the most important requirement is that the structure produced must support cell growth. One feature of such a porous arrangement is that it does not lend itself well to formation through molding. In addition, as a material will be contained within a biological environment, the polymer must be biocompatible. Thus materials such as gelatin are attractive for scaffolds as are polymers such as polyethylene glycol [XXXIII] and Poly (ϵ -caprolactone) [XXXIV]. The advantage of fused deposition modeling over the techniques described above is that it offers a mild route to the production of scaffold structures, and that no chemical modification is needed.



The way in which the rapid manufacturing process operates is likely to have a substantial bearing on the morphology of the final material. For example in the case of stereolithography where photopolymerization or photo cross-linking is involved (particularly with acrylates and styrene-based systems) a common result would be the production of a largely amorphous product with no anisotropy. Although as we have seen photo cross-linkable systems may contain crystallisable materials, in the case of fused deposition modeling, the use of a crystalline polymer is a simple matter; in addition it is released as a single filament (rather than the fused powder formed with selective laser sintering). Furthermore it may be that this level of crystallinity may be enhanced if the polymer is extruded, as in the system we discuss below.

Many polymeric materials such as polyethylene, polypropylene and poly (ϵ -caprolactone) exhibit semi-crystalline structures and the level and distribution of the crystalline phase is critical to the definition of the properties of the final product. Figure 5.11a contrasts the wide-angle scattering for atactic-polystyrene widely employed in photo-cross-linking resins with that for poly(s -caprolactone).

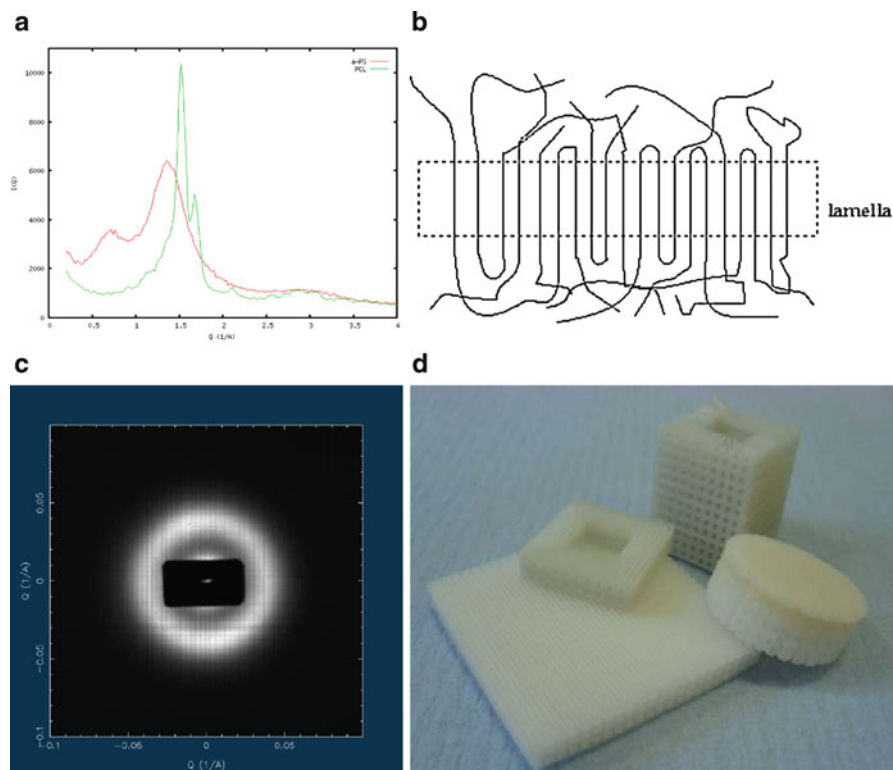


Fig. 5.11 Semicrystalline polymers: (a) Wide-angle X-ray scattering patterns for amorphous polystyrene and crystalline poly(ϵ -caprolactone); (b) A end view schematic of a chain folded lamellar; (c) Small-angle X-ray scattering of poly(ϵ -caprolactone) showing the scattering from the chain folded lamellae and (d) scaffolds for tissue engineering prepared by a layer addition system involving melt extrusion

The polystyrene curve shows broad peaks typical of an amorphous material. In contrast, the data for poly(ϵ -caprolactone) show sharp peaks arising from the significant fraction of crystalline material. These crystals are present in the form of thin chain folded lamellae (Fig. 5.11b) typically 10–20 nm in thickness, as confirmed by small-angle X-ray scattering techniques (Fig. 5.11c), but extending over micrometers in the lateral direction. Crystallization can take place in the solid state, but this is very unusual. Normally crystallization takes place either on cooling from the melt phase or precipitation from solution. It is difficult to see how the crystallization processes could be incorporated in to any effective stereolithography process. Hence semicrystalline polymers are excluded from the list of available materials for stereolithography unless added as a particulate. In contrast, the fused deposition system and other melt extrusion processes are particularly suited to semi-crystalline systems. A particular example of this approach is provided by bioextrusion; Fig. 5.11d shows an example of scaffolds produced by the bioextruder at Leira in Portugal [58]. The molten thermoplastic

is extruded by means of piston through a nozzle and deposited layer by layer to form a solid on cooling. The semi-crystalline structure can be optimized through variation of the temperatures and writing speed.

Fused deposition molding is one of a range of similar techniques in which 3D structures are built up through the deposition of material; for example inkjet printing has been used to produce scaffold structures from polyurethane [59]; other methods include laminated object manufacturing [39], and the pressure assisted microsyringe [60]. These techniques have their own material requirements and fit to particular application but the basic principles of material application layer by layer to form a 3-dimensional structure remains.

5.8 Conclusions

Rapid manufacturing offers considerable opportunities; the earliest applications of this technique were to produce prototypes to test designs; however, the methodology, in particular with improvements in computer technology has been extended to small scale production. Two particular applications stand out. The first is in biomedical applications – here the individuality of each situation is such that large scale manufacturing of parts is inappropriate. The second, which has increasing potential, is the situation where small scale manufacture of parts is required. In such situations machining parts may be very expensive; rapid manufacturing offers considerable commercial advantages. The challenge lies in the materials used. In many applications (particularly but not confined to biomedical solutions) properties such as mechanical strength or surface quality are important. The technology is rapidly improving, but considerable challenges remain, for example two-photon photochemical polymerization is being explored as a route to high resolutions and nanoscale device production [61]. As stated above materials are being improved including the production of composites [47, 57], such that the process better resembles manufacturing rather than prototyping, but in addition to this materials are being developed which will allow the prototype to be used to produce a mold, or indeed the technique has been used to make the molds. Many challenges remain but the importance of the approach to industry is such that the advances are likely to be as rapid as those over the past 20 years.

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