

Synthesis of High Temperature Resistant Polymers*

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Introduction

In order to make a polymeric material useful and servicable at elevated temperatures say about 300°C several conditions have to be met. First of all, the material must maintain its mechanical properties, such as rigidity, tensile strength and impact strength as a matter of instantaneous response, which means essentially, that it must not *melt* or *drastically soften* in that temperature range. If somewhat longer periods of service are involved it also becomes necessary that the *creep* of the polymer under the influence of the existing external forces, such as shear stress, torques or pressure should be sufficiently *slow* in order to permit its proper functioning. At still longer times chemical phenomena start to interfere, which may concern the polymer alone or which may involve other ingredients such as oxygen, acids, bases, organic reagents and also active radiation from the near ultraviolet to the cosmic rays. These processes may (and do) change radically the chemical structure of the material and, as a consequence, make it lower softening, increase its rate of creep, render it more brittle and reduce its mechanical strength to a very marked degree. In a certain (somewhat oversimplified) way one can, therefore, classify the conditions which are necessary for outstanding polymer stability:

- High melting or softening temperature.
- High resistance against spontaneous pyrolysis.
- High resistance against degradation through the action chemical reagents.

Let us briefly review these factors:

a) High Softening Polymers

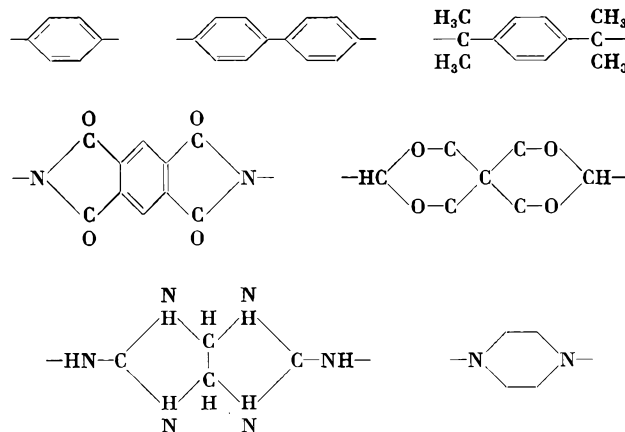
Experience as well as theoretical considerations indicate that there are essentially *two* ways to arrive at high softening systems: *crystallization* and *crosslinking*. The first approach leads to thermoplastic materials, which have a more or less sharp and reversible melting point, the second produces three dimensional, infusible networks which are thermosetting and can support very high temperatures without softening.

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High melting crystalline polymers are made from linear macromolecules, which are specifically designed to favor the formation of crystalline areas. The most important conditions are:

- Rigidity of the backbone chain.
- Regularity in the positions of the substituents.
- Strong interchain forces of the Van der Waals or hydrogen bonding type.

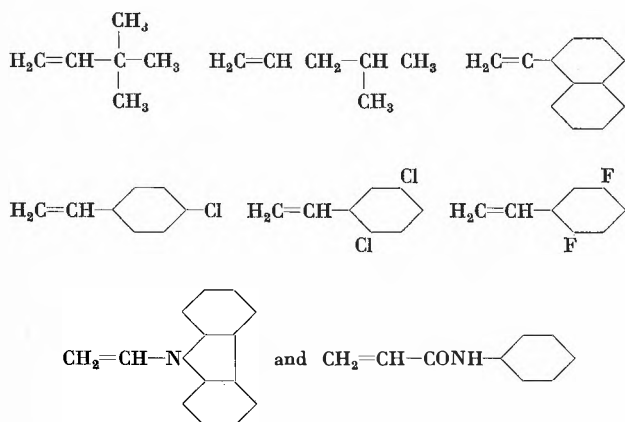
Rigidity of the backbone chain can be produced either by putting inflexible ring systems into the backbone or by affixing to it bulky and voluminous substituents. All present experience indicates that the first method is preferable because the presence of large substituents reduces the rate of crystallization of the macromolecules to such an extent that the materials remain amorphous even through the substituents are stereoregulated and all steps for favorable crystallinity, such as orientation and annealing are taken. A few examples for ring systems which have pronounced chain stiffening character are:



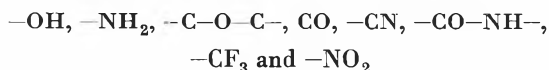
These elements can be incorporated into the macromolecule by addition or condensation and, in the latter case by ester, amide, acetal, anhydride, urethane or ureid bonds. A large number of polymers have been made where one relies essentially on the chain stiffening principle; some of them have melting points up to 400°C, but relatively rapid *creep* sets in at already substantially

lower temperatures and there is also a certain tendency for environmental *stress cracking*.

The principle of stereoregulated substitution with carbon-carbon or carbon-oxygen backbone chains has only been available for the synthesis of polymers since the discoveries of ZIEGLER and NATTA but has already to interesting cases with melting points up to 300°C. Some examples are the stereoregulated species of alpha olefins such as of



The principle of strong intermolecular bonding requires the introduction of polar or hydrogen bridging groups; the most important of them are:



Some of these groups can be either members of the main chain or substituents, others can only appear as substituents pending off the backbone chain. But, in any event, these groups increase the average cohesive energy density of the polymer and raise its melting or softening range. Because of their polar viz. hydrogen bonding character they also affect very profoundly the compatibility of the material with small organic molecules which manifests itself in solubility, plasticizer acceptance and moisture regain.

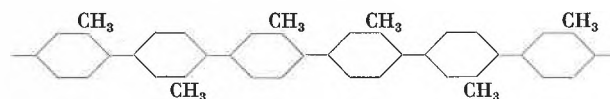
In practice, one does not rely only on *one* of these three possibilities but tries to operate with a superposition of them in such a manner that one does not push any single principle to its extreme but rather attempts to strike a compromise between them, which leads to the best combination of desirable properties.

Thus a polyphenylene



is very crystalline and high melting but even low molecular weight species of this series are so insoluble that nobody has, as yet, succeeded pushing the degree of polymerization high enough so as to obtain reasonable me-

chanical properties. If one introduces $-\text{CH}_3$ groups at the rings and prepares a polytolylene



the crystallinity and the softening range decrease noticeably but, at the same time, the solubility in hot hydrocarbon solvents increases which permits to maintain the reaction into the range of higher polymerization degrees and allows to prepare filaments and films from solutions of these polymers.

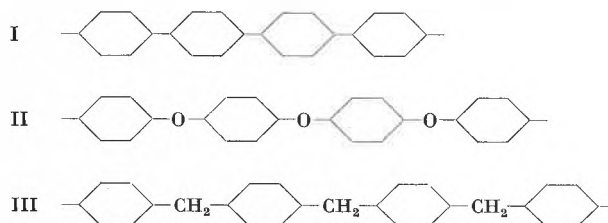
b) Thermal Stability of Polymers

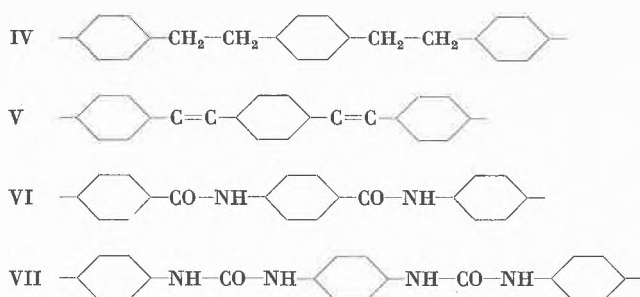
There are two processes which change the mechanical behavior of a polymer if it is exposed to such high temperatures that *chemical* changes are taking place: *degradation* and *crosslinking*. The first process is caused by scission of the chain molecules and, if occurring alone, leads to a progressive reduction of the molecular weight and with it to a loss in strength, elongation and toughness, to a decrease in softening temperature and increase of creep. The second process, if occurring alone, results in the formation of bonds *between* the individual polymer chains, ties them into a more and more rigid network, increases the molecular weight and leads to a very hard and brittle product which can neither be melted nor dissolved.

In many cases both processes occur simultaneously which can have the consequence that they balance each other for a while which may create the impression as if no changes were taking place at all. Sooner or later, however, one of the two reactions starts to prevail and one arrives either at a drastic softening or at a drastic embrittlement of the material.

The primary steps to both processes degradation and crosslinking is the formation of free radicals either by the breaking of a carbon-carbon bond: $-\text{C}-\text{C}- \rightarrow -\text{C}\cdot-\text{C}-$ or by the formation of H_2 from two adjacent CH_2- groups: $-\text{CH}_2-\text{CH}_2- \rightarrow -\dot{\text{C}}\text{H}-\dot{\text{C}}\text{H}- + \text{H}_2$. Considering the stability of a polymer to pyrolysis it is obvious that one should avoid the presence of any longer sequence of $-\text{CH}_2-$ groups and to rely on cyclic structures of the aromatic type which are well known to have a superior stability also in the low molecular weight range.

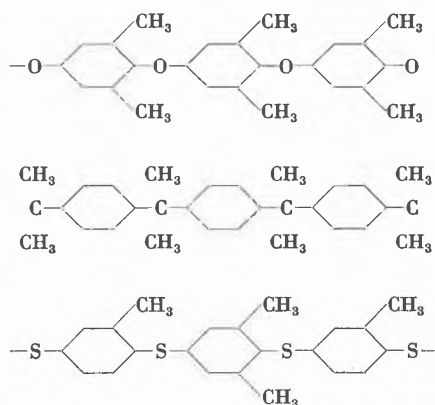
The interest centers therefore on such systems as:





and on derivatives of them. Most of these structures have been obtained in the form of *low molecular weight* species, have exhibited *high resistance* against pyrolysis but *have not shown any useful mechanical properties*. The problem obviously is how to *penetrate into higher molecular weight ranges*. One way appears to be the introduction of substituents such as CH_3 or Cl in the cyclic parts, which increases the *solubility* of the macromolecules and permits the reaction to proceed to higher degrees of polymerization. Another approach is given by the technique of *interfacial polymerization* where very high molecular weight products are formed at an interface even though they are not soluble in either of the liquids. Still another possibility to arrive at high molecular weight species of insoluble and infusible polymers appears to exist in *solid state polymerization*.

A few high molecular weight polymers of this type with good thermal stability which have been produced recently are:

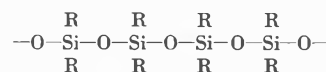


It is reasonable to expect that others will follow and that, eventually, polymers will be prepared which combine high temperature stability with good and even excellent mechanical properties.

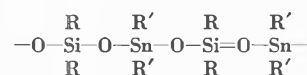
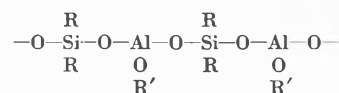
Another principle to improve thermal stability is the replacement of all (or most) hydrogen atoms by fluorine; it has already been carried out with great success in the synthesis of Teflon, Kel-F, Viton and other polymeric fluorocarbons and is particularly effective if lateral bonds between the chains are introduced with the aid of organic or inorganic crosslinking agents.

Still another, very effective and promising way to arrive at macromolecules with increased thermal stability

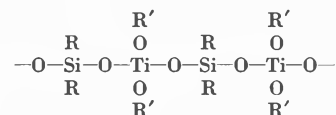
is the introduction of inorganic elements, such as Si, P, Mg, Al, Ti, Sn either in the backbone chains or in the substituents. The first representatives of such systems are the well known silicone polymers or polysiloxanes of the general formula



where R can be CH_3 , C_2H_5 , C_6H_5 or CF_3 . Although the intrinsic thermal stability of these polymers is very good they suffer under a certain weakness because there exists the tendency of an equilibration of the chains into rings with 8, 10, 12 and 14 members, which increases with increasing temperature and eventually leads to a progressive softening of the material and to a complete loss of toughness, strength and elasticity. This tendency can be reduced by the introduction of other elements into the backbone chain, such as Al, Ti or Sn which leads to polymers of the general form



and

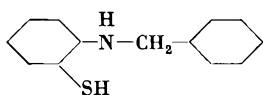


Systems of this type can be crosslinked and represent materials with excellent stability against thermal degradation and deterioration by ring formation, but, here again, the mechanical properties are still unsatisfactory because of insufficient degree of polymerization of the samples.

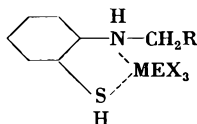
Another method to improve the thermal stability of organic polymers is the introduction of heavy metals in the form of ions into carboxyl or sulfoxyl groups; examples for such cases are the tin salt of polymethacrylic acid and polystyrene parasulfonic acid and corresponding compounds which contain phosphorous, titanium and antimony. In these cases the inorganic elements do not only raise the temperatures of softening and decomposition but they also act as very efficient flame proofing ingredients.

Another interesting application of inorganic elements (specifically heavy metal compounds) in organic polymers is based on the idea to use bifunctional chelating compounds as units in the building up of a macromolecular chain. If aromatic systems are used, one arrives at very high melting and stable combination. Let us give one example for this principle: If one reacts anilin with

toluene and sulfur, there results a condensation product of the formula



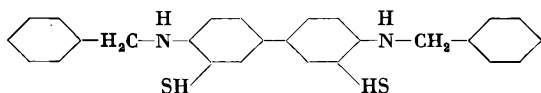
which has been synthesized long ago as an intermediate for certain dyestuffs. Its coloristic properties are based on the fact that many heavy metal salts form a chelate type complex with the NH and SH groups in the *ortho* position



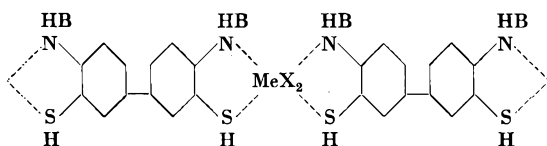
where X can be Cl or any other substituent at the metal.

These compounds are deeply colored, have strong affinity to many fibers and are very stable at elevated temperatures. In fact their lightfastness and heat resistance approaches that of typical pigments such as the metallized quinacridones and phthalocyanines.

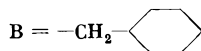
This has stimulated the idea to replace the aniline component by benzidine or *para*-phenylene diamine and to combine chelation with bifunctionality by starting with



This molecule evidently has two chelating positions and can form a linear macromolecule if it is allowed to react with a chelating metal compound. The chain, which results has the following structure



where

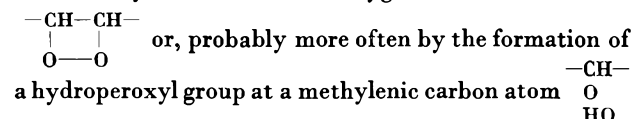


This principle obviously permits many variations concerning the structure of the organic component and the choice of the metal salt. Several recent attempts have shown that «chelate polymerization» does occur, but, at present it has not yet been possible to penetrate into the domain of sufficiently high degrees of polymerization to obtain reasonably good mechanical properties. The thermal stability of the oligomers (DP between 4 and 8) was satisfactory so that it can be hoped to arrive at interesting new polymers as soon as one succeeds to build up sufficiently long chains.

c) Stability Against Chemical Agents

One important property for many uses of polymeric materials is their stability against hydrolytic changes and degradation either by water or steam alone or by the action of acids and bases. Two different types of such influence can be distinguished. If the hydrolyzable bond is located in the backbone chain, as in the case of a polyester, polyamide or polyurethane, the hydrolytic action consists in a degradative effect which reduces the molecular weight more or less drastically and leads to a progressive deterioration of such important properties as tensile strength, impact strength, extensibility and abrasion resistance. If, on the other hand, the hydrolyzable bond links a substituent to the main chain as it is the case of cellulose-acetate, polyvinylacetate or polymethacrylate, the result of hydrolysis is a more or less pronounced change in the *chemical* character of the material, which is accompanied by changes in solubility, swelling characteristics and chemical reactivity. An ester or an amide is converted into an acid or an alcohol, with the corresponding consequences for the physical and chemical behavior of the system.

Another dangerous reagent causing deterioration of polymers is oxygen and/or ozone particularly at elevated temperatures and in the presence of ionizing radiation. The reaction steps which produce degradation or cross-linking (or both) are essentially of the free radical type, initiated by the addition of oxygen to a double bond



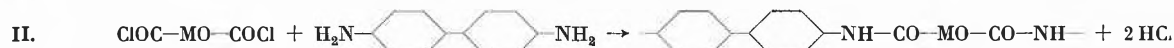
This group in turn decomposes into a hydrogen atom and ROO^\cdot or into a hydroxyl radical and RO^\cdot whereupon a chain of radical reactions follows, which can lead to chain scission, branching or crosslinking and which, in any event, deteriorate the mechanical properties of the material. In order to reduce the danger of such attacks to a minimum, it is necessary to avoid the presence of any multiple bonds in the system and also the presence of any methylene groups, which are activated by electron density releasing neighbors. This leads again to structures of aromatic rings, which are linked together by short chains in such a manner that there exists a throughgoing or almost throughgoing stabilization by resonance. Thus the conditions for high stability against oxidation are rather similar to those which cause high softening characteristics and which protect the polymer against direct pyrolysis. On top of the choice of a particularly suitable structure one always improves the stability of a polymer against oxidation by the addition of an oxygen scavenger which reacts with it in preference to the polymer and also by the addition of a UV absorber which reduces the effect of ionizing radiation. However, even with the use of all these principles it still must be admitted that the combined influence of oxygen, light and heat is the most dangerous deteriorating influence on all polymers.

In the following paragraphs specific comments and recommendations will be made which are based on the principles presented in this introduction and might help to arrive at some improved compromises of thermal and mechanical properties.

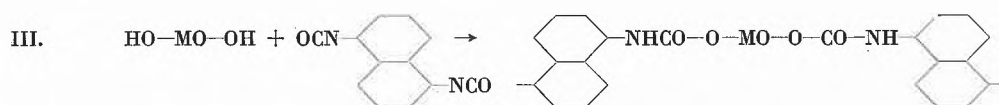
A review of the existing efforts to use Metal organic systems such as phthalocyanin, ferrocene and related materials to build up thermostable polymers with attractive mechanical properties indicates that thermal stability as such can be reached but that the mechanical properties are still far from being satisfactory. In fact, most materials are friable powders or as it has been said they are an expensive type of *brick dust*. Everything indicates that this is due to the *low molecular weight* of these materials, which, in many cases, is apparently around or even below 1000 and only in a few instances reaches such figures as 2000 or 3000. Adequate mechanical properties, however, can only be expected at molecular weights well above 10000. In the continuation of this work, all efforts should therefore be directed towards the synthesis of higher molecular weight species. Specifically the following steps could be taken in this direction:

a) Synthesis of bifunctional derivatives of the metal-organic nucleus which could be used to promote interfacial polymerization. A few examples of such possibilities are given here.

A reactive *dichloro- or dibromo-derivative* of the metalorganic nucleus (MO) could be reacted inter-facially with a diamine:



A *hydroxylderivative* of MO could be reacted interfacially with a diisocyanate

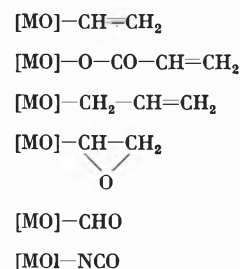


An aminoderivative of MO could be reacted interfacially with a diacylchloride



There exist many other possibilities but I suggest to try out one or two of the most promising (maybe I and IV) to find out whether this method *does give* higher molecular weight polymers.

b) *Solid state polymerization* of polymerizable MO-derivatives initiated either by an *ionic catalyst* (LiH, CaH₂, BaO or Sb₂O₃, TiCl₃, PbO₂) or by *ionizing radiation*. A few MO-derivatives which could give good results are:



If any of them could be synthesized it would appear that solid state polymerization could lead to a high molecular weight polymer.

Suggestions for other Approaches

Some of the best existing high temperature stable materials which have, at the same time, remarkable mechanical properties are *two component systems* in which a hard, high temperature resistant fine powder is embedded in a polymeric matrix to form fibers, films, coatings, plates and rods in which thermal and mechanical properties are combined in a very attractive way. In such cases the polymeric matrix is not supposed to act in bulk form but only in very thin surface layers as a *binder* between the particles of the *filler*.

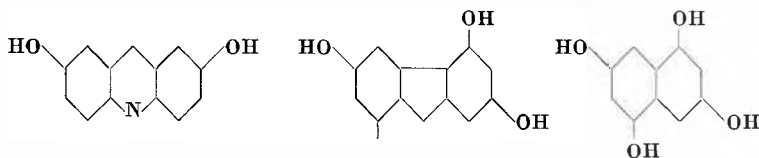
Useful *fillers* for such *two-phase systems* are graphite, other forms of finely divided carbon, SiC, BN and the nitrides of certain heavy metals.

As *binders* are, right now, used condensation products of formaldehyde with phenol, urea and melamine.

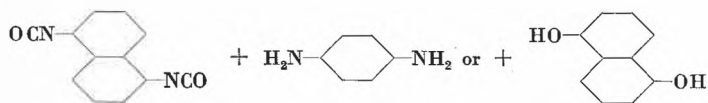
It appears that a systematic study of *polymeric binders* which permit to accommodate a *maximum percentage* of *fillers* (90 weight percent and more) and still give good mechanical properties should be promising. Its principle would be to entrust the high heat resistance essentially to the filler and use the thin polymeric layers of the binder only for the embodiment of mechanical strength.

Specifically the following filler systems could be recommended for investigation.

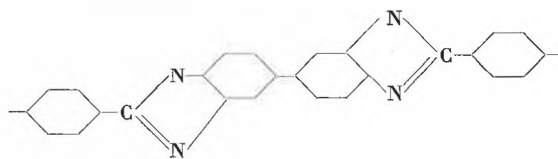
a) Phenolic compounds of higher condensed rings together with formaldehyde



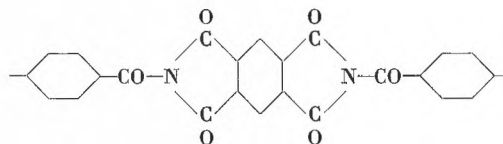
b) Aromatic isocyanates with aromatic amines or hydroxyl compounds



- c) Furfuryl alcohol and/or furfuryl aldehyde together with precondensation products of formaldehyde with phenolic materials, urea, melamine and cyanuric acid.
- d) Condensation products of aromatic tetramines with dicarboxylic acids



e) Condensation products of aromatic diimids with dicarboxylic acids



In all these cases the binder need not have a very high molecular weight to produce good mechanical properties of the final two phase-system so that many heat resistant polymers which cannot be used *alone* because of insufficient molecular weight can be successfully used as binders.