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Thermal Properties of Thermoplastics

Charles A. Wilkie

Marquette University, charles.wilkie@marquette.edu

Michael A. McKinney

Marquette University

4.2 Thermal Properties and Burning Behavior of the Most Important Plastics

4.2.1 Thermal Properties of Thermoplastics

C.A. WILKIE AND M.A. MCKINNEY

The combustion of any organic polymer involves several steps. The solid polymer must first be degraded to form small fragments, which can escape to the vapor phase. This involves an input of heat, either from an external source or by the feedback of energy from the already combusting material. These small molecules must now diffuse to the surface where they can escape and undergo further reactions to yield the actual species, usually hydrogen and hydroxy radicals, which make up the flame. The energy generated in this step is now fed back to continue the process.

This review is devoted largely to the chemistry that is involved in the degradation step of the combustion process. It is generally believed that oxygen plays an important role in the

combustion step, but not in the degradation step; the presence or absence of oxygen in the degradation step is unimportant. It is certainly true that degradation studies are quite dependent on the atmosphere in which the degradation is performed, and attention is paid to degradation in an inert atmosphere as well as in air.

4.2.1.1 Scope

This section covers the thermal degradation of various classes of thermoplastics as well as the methods used to study these degradations. The coverage is in no case encyclopedic, rather the section tries to provide enough information on the degradation of particular polymers or classes of polymers so that the reader will be able to decide if further literature work is warranted.

Thermoplastics include materials that soften when they are heated. Polymers that would be included are polyolefins, polybutadiene and other elastomers; PS and styrene-containing co- and terpolymers; poly(meth)acrylates; halogen-containing polymers such as PVC; and the fluorine-containing polymers such as polytetrafluoroethylene, polyamides, polyesters, and polycarbonates. The thermal characteristics of selected thermoplastics are summarized in Section 3 of the Appendix.

In general, the degradation of thermoplastics occurs by four mechanisms: random-chain scission, end-chain scission, chain-stripping, and other processes such as cross-linking. Scission involves the cleavage of a carbon-carbon bond in the backbone of the polymer to generate two radicals. This may be initiated at random positions throughout the polymer and give rise to a monomer and oligomers or it may be initiated strictly at the ends of the chain, end-chain scission. End-chain scission results in the exclusive formation of a monomer and is initiated at unsaturated chain ends.

In a random-scission reaction two radicals are formed from cleavage of the backbone of the polymer. One of these radical centers typically will be a methylene group, a primary radical, while the other will likely be on a carbon that whatever substituents are present in the polymeric unit will result in a secondary or tertiary radical. The reactive primary radical ordinarily will abstract hydrogen from a neighboring position to give a more stable secondary or tertiary radical, or from a more removed position, even on another polymer strand. This new secondary or tertiary radical can now undergo further degradation, typically by the formation of a new primary radical and an unsaturated species, as shown in Fig. 4.3.

End-chain scission occurs when hydrogen transfer is inhibited, for instance, if the substituents adjacent to the primary radical site are groups other than hydrogen atoms. Polymers such as

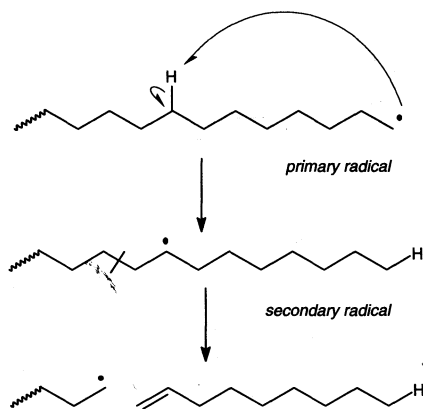


Figure 4.3 Intramolecular hydrogen transfer and β -scission process

PMMA, with methyl and carboxyl substituents, polymethacrylonitrile, with nitrile and methyl groups, poly(-methyl styrene), phenyl and methyl, are examples of polymers that undergo end-chain scission. If at least one of the substituents is a hydrogen, then random scission can occur with hydrogen transfer, and oligomers as well as monomers are produced. One method to differentiate between end-chain and random scission is based on the identification of the products. If only monomer is produced, it is quite likely that only end-chain scission has occurred.

The chain stripping process occurs when a small molecule, such as HCl or acetic acid, can be eliminated from the polymer. Thus polymers such as PVC, poly(vinyl acetate), and poly(vinyl alcohol) can eliminate HCl, HOOCCH₃, and H₂O, respectively, with the formation of a double bond in the main chain. One should recognize that these new polymeric structures containing double bonds can undergo subsequent reactions that may, or may not, be advantageous in the overall degradation scheme.

The other mechanism of degradation is a cross-linking process. The best known example of this process is in the degradation of polyacrylonitrile, which is discussed later in this chapter. Related to this cross-linking degradation pathway is the formation of char. One of the areas of active interest in the fire retardant community is the promotion of char formation because char offers the opportunity to insulate the polymer from the source of the heat and thus to inhibit the degradation processes.

4.2.1.2 Techniques to Study the Thermal Degradation of Thermoplastics

The techniques that are used in the study of thermal degradation pathways may be separated into two distinct categories based on the information desired: Scientific techniques are used to assess thermal stability and to provide data which can be used to determine the process by which a polymer degrades and commercial tests, which are performed in order to provide data, which can be used to enhance the salability of a particular product. The scientific techniques include TGA and related procedures and differential scanning calorimetry (DSC) and related procedures. One can couple any of these as a means of identifying products that evolve during the degradation to derive information on the course of the degradation.

In TGA, a sample of milligram size is heated, usually under an inert atmosphere, either isothermally or at a constant rate, and the mass of sample is followed as a function of either time or temperature. The degradation depends somewhat on the rate at which the temperature is increased and this must be taken into account in any investigation. In some cases the evolved gases are then analyzed, typically by mass spectroscopy or infrared spectroscopy. If the derivative of the mass loss versus temperature is recorded, this is called differential thermogravimetry (DTG). The main advantage of DTG is that the derivative enables one to determine more exactly the temperature at which some degradation is occurring.

Related to TGA is thermal volatilization analysis (TVA). The major practitioners of this technique are Norman Grassie and Ian McNeill. Here the sample is heated in a vacuum system, which has a liquid nitrogen trap between the sample and the vacuum pump. Any volatiles produced will increase the pressure in the system. Thus pressure is related to the rate of volatilization, and a sample transducer, not a balance, is used to measure the rate of degradation. The use of suitable traps enables one to trap all of the products, which are evolved for later analysis.

Another related technique is pyrolysis gas chromatography. The pyrolysis is carried out in the injector of the gas chromatograph and the volatile products that are formed flow through the chromatography column and can give a fingerprint of the degradation products. This technique is used for the identification of polymers and is used less often for mechanistic studies.

The aforementioned techniques give information on the rate of degradation but it is also of interest to obtain information on the heat involved in various thermal processes, that is, its endo- or exothermicity. Two techniques, differential thermal analysis (DTA) and DSC, are used for this purpose. The measurement is slightly different but both techniques provide information on the heat effects, which occur when a polymeric sample is heated.

Two more tests that more or less fall into the realm of scientific tests are the oxygen index (OI), also known as the limiting oxygen index (LOI), and cone calorimetry. Oxygen index measures the ease of extinction of a fire. A sample is ignited in an atmosphere that contains a known composition of nitrogen and oxygen and one measures the minimum oxygen concentration that is required for flame extinction, called the oxygen index. This can be very useful because by substituting another oxidizer, for instance nitrous oxide (N_2O), for oxygen, one can determine if an additive functions in the condensed or the vapor phase. A condensed mechanism will not show any variation with the identity of the oxidizer while a vapor phase reaction will be dependent on the oxidizer. Cone calorimetry measures the depletion of oxygen as a sample is combusted. One is able to measure the rate at which heat is released and mass is lost, as well as the evolution of smoke. Both of these tests are used primarily for commercial evaluation but there is some scientific component, as one can develop information that relates to the degradation pathway.

The commercial tests include measurement of ease of ignition, flame spread, rate of heat release, rate of extinction, smoke evolution, and evolution of toxic gases. Only one of these, the UL 94 test, which measures the ease of ignition of a polymeric sample, is referred to in this chapter. In this test, a series of samples are ignited and one observes if the sample continues to burn when the ignition source is removed; in addition dripping of the sample is important. The results of this test lead to a classification.

4.2.1.3 Thermal Degradation Pathways

Polyolefins. We consider only two systems in this classification, polyethylene (PE) and polypropylene (PP). Because both of these have hydrogen atoms on all carbons, one can expect that random scission will be the dominant pathway of the degradation and therefore one can expect to find monomer and oligomers as the products of the degradation. A TGA curve of low-density PE [1] shows that in a nitrogen atmosphere, degradation does not commence until the temperature is above 400°C while complete volatilization has occurred by 500°C . By contrast, in air the degradation begins at 235°C and rapid weight loss occurs above this temperature. The TGA of high-density PE [2] appears to show similar thermal stability characteristics. The onset of PP degradation begins at a somewhat lower temperature [2]. The principal products observed during the degradation of PE include ethylene and higher oligomers, which arise from hydrogen transfer to different positions along the polymer chain, thus one observes propylene, butene, pentene, hexene, and so forth, as well as a series of alkanes [3]. A degradation pathway for PE is shown in Fig. 4.4. The degradation of PP is more complex and a wider variety of products is produced. The major volatile products found in the degradation of PP, in order of importance are 2,4-dimethyl-1-heptene, 2-pentene, propylene, 2-methyl-1-pentene, and in much smaller amount, isobutene [4].

Recently Hedrick and Chuang [5] reported on a temperature-programmed reaction technique, coupled to *in situ* infrared and mass spectral analysis, to study the thermal degradation of PP. The degradation reaction is performed within the infrared cell and the evolved gases are analyzed by mass spectroscopy, infrared analysis, and gas chromatography. At the same time, infrared spectra of the solid material can be obtained. They observed similar products to those previously found but suggested a slightly different mechanistic pathway for the degradation.

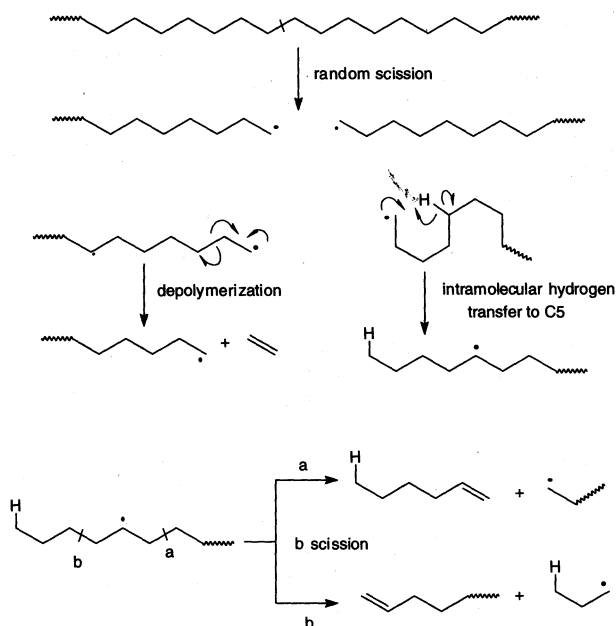


Figure 4.4 Degradation of PE showing initial random scission, depolymerization, intramolecular hydrogen transfer, and β -scission of the macroradical

Camino, Costa, and co-workers [6–13] investigated the effects of a chlorinated paraffin, either with or without a metal salt, on the thermal degradation of PE and PP. Several conclusions may be drawn from this work. The presence of the chlorinated paraffin alone increases the fraction of low molecular weight (C-1 to C-4) saturated hydrocarbons and decreases the fraction of olefins formed from both PP and PE. It has been speculated that this may occur by the reaction of hydrogen, which is eliminated from the degrading chloroparaffin, interacting with olefins to give saturated species. In the presence of the chlorinated paraffin, PE undergoes a cross-linking reaction while PP becomes subject to degradation. The observation that the N_2O index shows the same slope as the concentration of the chlorinated paraffin is changed for PE as does the oxygen index indicating that fire retardant effects occur in the condensed phase. For PP, the slope is similar but not exactly the same and this implies that both condensed phase as well as vapor phase effects are occurring. The degradation of PP in the presence of both the chlorinated paraffin and a metal salt, either antimony oxide or bismuth carbonate, shows that synergism occurs between these components. Surprisingly the combination with antimony oxide functions in the vapor phase while that with bismuth carbonate shows condensed phase activity.

The Italian Turin group has also extensively investigated an intumescence system with PP [14–19]. The French group from Lille has also played a major role in developing the understanding of intumescent systems [20, 21]. Members of both of these two groups have recently authored an authoritative review on intumescence [22]. The normal intumescent system consists of an inorganic acid or its precursor, a polyhydric compound, which acts as the source of carbon for char formation, an organic amine or amide, and a halogenated organic compound. Intumescence involves more than a single physical effect and it is believed that one of these effects is to produce char by dehydration of the polyhydric compound catalyzed by the acid, and this char is then blown by volatile components evolving as the amine or halogenated compound are heated. In this work they used the combination of ammonium

polyphosphate and pentaerythritol, sometimes also using melamine or its salts. If one compares the TGA curve of PP with that of a mixture of PP with ammonium polyphosphate and pentaerythritol, one sees that the calculated and experimental mass loss curves are in agreement up to 460°C. At higher temperatures a lower mass loss is found than calculated and a larger amount of char is formed at 500°C. The fraction of PP that degrades is reduced in the presence of the additive. This is believed to be strictly a physical effect in which the foamed char prevents heat from causing further degradation and a chemical effect in which the char traps the polymer degradation products and as a consequence prevents the fuel transfer to the flame.

There have been two reports on PP nanocomposites [23, 24]. These materials are formed using a montmorillonite clay together with PP-graft-maleic anhydride (PP-g-MA). The maleic anhydride is necessary to make the polymer and the clay compatible. The peak rate of heat release is lower by more than 50% in the nanocomposite compared to virgin PP-g-MA.

Diene Polymers: Polybutadiene (PBD), Polyisoprene (PIP), and Polychloroprene (PCP). Once again, these polymers have at least one hydrogen on all carbons and degradation will occur by the random scission process so one expects to observe monomer and oligomers. In the case of PCP, the presence of the chlorine atom means that the possibility to eliminate a small molecule, HCl, is present, so one may expect that chain-stripping will occur for that polymer. The three polymers show quite different thermal behavior. PBD is the most stable, with degradation commencing at about 450°C [25]. The TGA curve for PIP shows that degradation begins below 350°C [26] while in PCP there is some degradation as early as 200°C but the main degradation occurs between 300 and 450°C [27]. The lower thermal stability of PCP is likely related to the possibility of chain-stripping as a degradation pathway for this polymer but not for the other polymers.

The products from the thermal degradation of PBD include monomeric butadiene and a small amount of aromatics arising by coupling of the oligomeric fractions that are produced [28–30]. Similar products are to be expected from PIP. The DSC curve of PBD shows that *cis-trans* isomerization occurs at a temperature as low as 200°C, well below the temperature at which mass loss is observed. On the other hand, PIP shows negligible isomerization below 350°C. It has clearly been shown that cross-linking of PBD occurs during the course of a TGA [29, 31]. The degradation of PCP has been studied by thermal volatilization analysis and it was found that the major product that evolved was hydrogen chloride [27]. Ultimately, about 90% of the available chlorine is lost as HCl and this will lead to the formation of double bonds along the polymer chain, which can cross-link [32]. The scheme shown in Fig. 4.5 has been proposed to account for the depolymerization and cross-linking of PBD [29].

Work has been carried out on the cross-linking of PBD and related polymers using chemical initiation [31] and high-energy irradiation [33]. When PBD is cross-linked, regardless of the process used, it undergoes an earlier thermal degradation than does the virgin polymer. It has been shown in this work that PBD will cross-link under TGA conditions and the resulting material has a higher cross-link density than is obtained by either irradiation or chemical cross-linking.

Polystyrene (PS) and Its Terpolymer Acrylonitrile-Butadiene-Styrene (ABS). Coverage here is limited to PS and the terpolymer acrylonitrile-butadiene-styrene (ABS). The degradation of PS has been extensively studied; again the degradation proceeds by a random scission process. The degradation begins at about 360°C and is complete by 450°C; the observed products are styrene and its oligomers along with benzene and toluene [30, 34–38]. The degradation of ABS begins at 340°C with the formation of butadiene monomer and aromatics are first noted at 350°C. As the temperature is raised, styrene and its oligomers become more prominent. At the highest temperatures, aromatics decrease in intensity but butadiene remains strong throughout the course of the degradation. The evolution of acrylonitrile is also noted [30]. As

monomeric acrylonitrile is not seen in the degradation of polyacrylonitrile, its observation here may be a surprise. As discussed later, the degradation of polyacrylonitrile occurs by a cross-linking pathway in which one nitrile nucleophilically attacks the adjacent unit to give a cyclized structure. In styrene-acrylonitrile, which is the precursor of ABS, acrylonitrile units are not adjacent so such attack cannot occur and the monomer is observed instead.

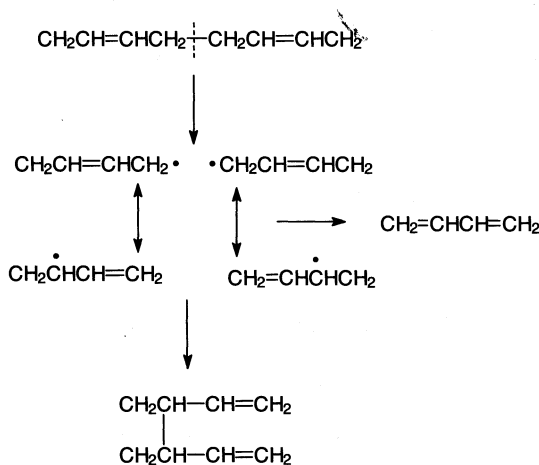


Figure 4.5 Formation of monomer and cross-linking from degradation of polybutadiene

A recent article covers the thermal degradation of cross-linked PS, prepared using varying amounts of divinylbenzene together with styrene [39]. The onset temperature of the degradation is increased as the cross-link density increases and up to 10% of these cross-linked polymers are non volatile at 600°C.

Halogenated compounds are the normal additive for PS and the work discussed in the preceding paragraphs using chlorinated paraffin for PE and PP has also been applied to PS. The behavior of PS is identical with that of PE in this regard.

Recently a new procedure has been introduced to enhance the fire retardancy of PS, based on Friedel-Crafts chemistry. In early work, it had been shown that one can cross-link PS using Friedel-Crafts chemistry but at low temperatures where processing will be impaired [40–42]. Recent work has shown that one can cause the cross-linking reactions to occur only when the PS is heated to 250 or 300°C [43–45]. Cone calorimetry and radiative gasification studies on this system have shown that the rate of heat release is decreased by 60% and that this effect occurs because char is formed at the surface, which protects the underlying polymer from further degradation.

Weil et al. [46] have shown that potassium carbonate is a good flame retardant, as measured by oxygen index, for both ABS and high-impact polystyrene (HIPS). The effect is due to oxidative crosslinking of the butadiene component of both polymeric systems. Gilman et al. [23, 24] have prepared intercalated nanocomposites of PS and again observed that the peak heat release rate is significantly lower for the nanocomposite than for the virgin polymer.

Poly(meth)acrylates. The degradation of PMMA gives essentially only monomer by a random-chain scission. At least two and sometimes three stages of degradation are evident from a TG study of the degradation. From the earliest work in this area, these stages have been attributed to reactions at the chain ends and a random scission process producing only monomer [47–50]. All of the available information leads one to believe that degradation of PMMA proceeds to form only monomer, but little information is available to explain how the

reaction occurs. Hodder et al. [51] examined the thermal degradation of a copolymer of MMA and MMA- d_8 to see if scrambled products were produced. If the two ends of the monomer that were initially joined become reattached in the degradation, no scrambled product results; however, if the tail from one unit is attached to the head from a different unit, scrambled product would result. The monomer products that they obtained were completely deuterated or completely undeuterated; therefore no scrambling had occurred.

Kashiwagi et al. [52] have shown by TGA that a radically polymerized sample degrades in three stages, at approx. 165, 270, and 360 °C, whereas an anionically polymerized sample degrades in only one stage, at 360 °C. Because the anionically polymerized sample should contain no weak links, they propose that the single degradation pathway observed for this sample is the result of the random scission process. They suggest that the first step is due to the presence of head-to-head linkages present in the sample and attribute the second step to unsaturated chain ends. The instability of the unsaturated chain ends and of the head-to-head linkages has been confirmed by Meisters et al. [53]; however, they report that the head-to-head linkage is more stable than the unsaturated end groups. Another problem regarding the instability of the head-to-head linkage is the question of diffusion. For degradation to occur from a head-to-head linkage, the two radicals must diffuse away rather than recombine. There is some evidence to suggest that the diffusion of these radicals is very slow and that recombination is much more likely [54].

Any scheme that invokes random scission as the initial step must produce both a primary radical as well as a tertiary radical and both must degrade to give identical products. The tertiary radical will likely unzip, but unzipping of the primary radical is considered unlikely. Both Kashiwagi [55] and [56] have considered this problem and both have proposed Manring that side-chain scission is a viable initial step in the degradation process. Kashiwagi suggests that the primary radical undergoes β -scission with the formation of a methoxycarbonyl radical and unsaturated PMMA oligomer. This last oligomer then will degrade by the route known for PMMA molecules with terminal unsaturation. On the other hand, Manring suggests that the original step in the degradation process is side-chain cleavage with the direct formation of a methoxycarbonyl radical and the unsaturated polymer.

These mechanisms are virtually identical. Kashiwagi's process begins with a main-chain scission followed by a side-chain scission whereas Manring's mechanism requires an initial side-chain scission followed by the main-chain scission. The degradation pathway, following the Kashiwagi scheme, is shown in Fig. 4.6.

Degradation of cross-linked MMAs has also been studied [39]. These cross-linked materials were prepared using four different dimethacrylates, three of which are aliphatic and one, bisphenol A dimethacrylate, aromatic. The onset temperature of the degradation is lower for the cross-linked polymers than for PMMA. Insignificant char formation is observed for the polymers cross-linked using the aliphatic dimethacrylates but the amount of char does appear to increase for the aromatic system. As carbonaceous char is graphitic in character, the aromatic material is closer to what is required and produces char more easily.

When esters other than methyl are studied, ester decomposition with the formation of olefin and the acid becomes an important reaction. For poly(*n*-butyl methacrylate), approx. 30–50 % of monomer is formed and poly(ethyl methacrylate) behaves similarly [57]. Ester decomposition is the principal degradation pathway for poly(*tert*-butyl methacrylate) and the major volatile products are isobutene and water (from the degradation of poly(methacrylic acid) (PMAA) [58]. The degradation pathway for all esters is a tradeoff of these two processes.

The degradation of PMAA occurs in two stages. In the first stage, at 150–250 °C, water is lost and poly(methacrylic anhydride) is formed. The second stage, which involves degradation of this polymeric anhydride, begins at about 300 °C and is complete by 450 °C. Ho et al. [59] have studied both stages kinetically and have also proposed a mechanistic scheme for the degradation of the anhydride.

There have been several publications on the degradation of salts of PMAA [60–63]. In general, the salts are stable up to approx. 350°C. The principal degradation products include monomer and the corresponding isobutyrate, carbonate, oxide, carbon dioxide, and a collection of volatiles, which include several aldehydes and ketones. The stability of the metal carbonate controls the course of the reaction to a certain extent.

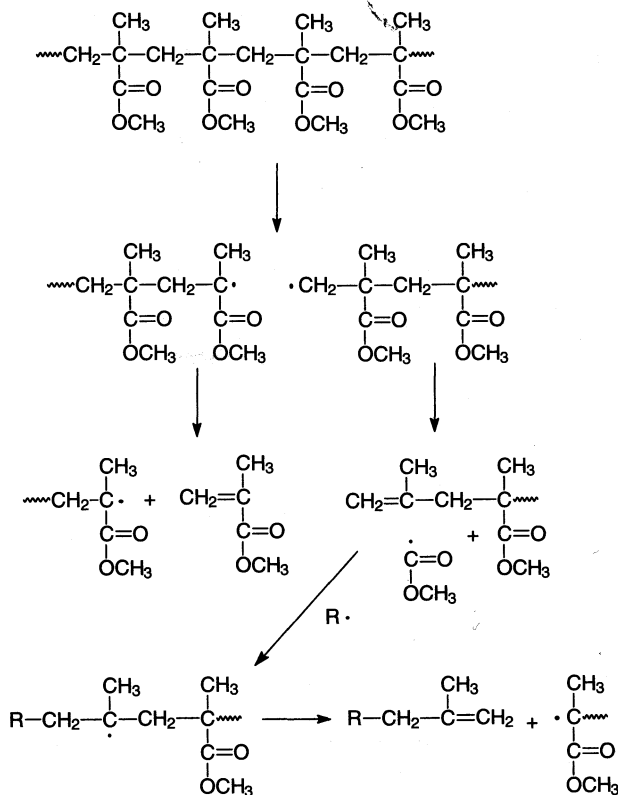


Figure 4.6 Degradation pathway of PMMA

The degradation of polyacrylates is quite different from that of the corresponding methacrylates because of the difference between a methine carbon in the acrylate and the quaternary carbon in the methacrylate. The degradation of PMMA produces 100% monomer whereas acrylate gives perhaps 1% monomer, and the main products are those due to random chain scission, namely oligomeric fragments. Just as for methacrylates, higher acrylate esters also undergo the ester cleavage reaction to give olefin and poly(acrylic acid) (PAA).

The degradation of PAA is qualitatively similar to that of the methacrylic acid in that water loss with the formation of anhydrides occurs. Various oligomeric acid and anhydride structures are also produced [64]. The degradation of salts appears to follow a similar pathway [65].

A significant amount of work has been carried out on the interaction of PMMA with additives; additives that have been examined include silver acetate [66], red phosphorus [67, 68], zinc bromide [69, 70], Wilkinson's salt, $(\text{PPh}_3)_3\text{RhCl}$ [71, 72], $\text{Ph}_x\text{SnCl}_{4-x}$ ($x = 0-4$) [73, 74], Ph_2S_2 [75], Nafions [76], various transition metal halides [77–79], metal acetylacetonates [80,

81], and copolymers of MMA with 2-sulfoethylmethacrylate [82]. The focus of this work has been to develop a mechanistic understanding of the effects of the additive on the degradation of the polymer. To enhance the thermal stability of the polymer, one must either prevent the initial degradation or capture the products of this degradation so they cannot undergo further reaction.

Polyacrylonitrile (PAN) and Polymethacrylonitrile (PMAN). An examination of the formulas of these two compounds explains the great differences in their degradation pathways. PMAN has two substituents on a carbon atom and thus will undergo end-chain scission with the formation of a large fraction of monomer, while PAN degrades via a cross-linking pathway to give only very little monomer [83]. The degradation of PAN has been of interest owing to the possibility of generating carbon fibers from its degradation. We have recently reviewed the literature on this degradation and proposed a pathway by which the volatile species, ammonia and hydrogen cyanide, are evolved [84]. The essentials of the scheme to account for the evolution of ammonia involve cyclization by nucleophilic attack of an end group on an adjacent nitrile to give a ring structure. This is followed by tautomerization, isomerization, and elimination of ammonia and hydrogen to give the graphite-like char known to be produced. Only small amounts of HCN are produced and this may arise from either the presence of head-to-head linkages or a radical process in which cyanide radical is eliminated. It should be noted that the degradation of styrene-acrylonitrile copolymer is quite different as the acrylonitrile units are randomly arranged and the nucleophilic attack that leads to ring formation cannot occur and monomer is instead eliminated.

The thermal degradation of PMAN has been studied by Metcalfe et al. [85] and they report that, in addition to methacrylonitrile, hydrogen cyanide, propyne, propane, butene, acetonitrile, acrylonitrile, propionitrile, benzene, crotonitrile, pyridine, toluene, cyanobutene, styrene, benzonitrile, indene, methyl benzonitrile, and ethyl styrene are produced. It is interesting that the fraction of methacrylonitrile formed decreases as the temperature at which the combustion is performed is increased while hydrogen cyanide evolution increases. At 700°C 64% acrylonitrile and 2% HCN are produced, while at 900°C 64% HCN and 0.1% methacrylonitrile are obtained. This suggests that HCN is a secondary product that arises from the degradation of the primary products, and several mechanisms were proposed to account for its production.

Poly(vinyl chloride) (PVC) and Related Materials. It is quite simplistic to state that PVC degrades by chain-stripping with the loss of hydrogen chloride, as this reaction yields additional products that can participate in further reaction, mainly cross-linking. Degradation and stabilization of PVC has been reviewed by Tran [86]. The chain-stripping commences at temperatures as low as 100°C and is autocatalytic. The double bonds that are formed are conjugated and can give rise to aromatic structures that will burn with the formation of significant quantities of smoke. A scheme has been proposed to account for the autocatalytic character of the degradation, as shown in Fig. 4.7 [87].

The cross-linking reaction can be prevented by heating in the presence of maleic anhydride, which suggests that a Diels-Alder type of cross-linking occurs, as shown in Fig. 4.8.

Further reactions of the polyenes produced by loss of HCl determine the course of the PVC degradation. If the cyclization reactions noted in the preceding occur, the aromatics, largely benzene, that are produced, burn in the vapor phase with the formation of large amounts of smoke and the heat generated in the combustion facilitates further degradation. On the other hand, if the polyene sequences continue to undergo cross-linking, then char formation occurs and the production of aromatics, with their inherent char, is reduced and the material is stabilized [88-93].

Anthony [94] has recently constructed a kinetic model that fits the TGA curve reasonably well. The model involves the initial loss of hydrogen chloride to give a polyolefin. The poly-

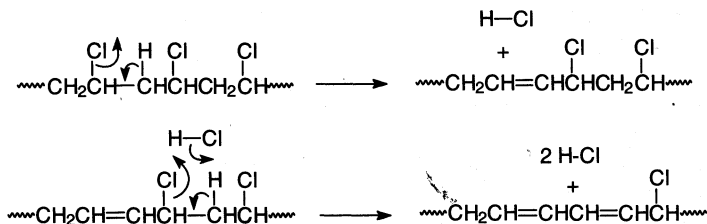


Figure 4.7 Autocatalytic degradation of PVC

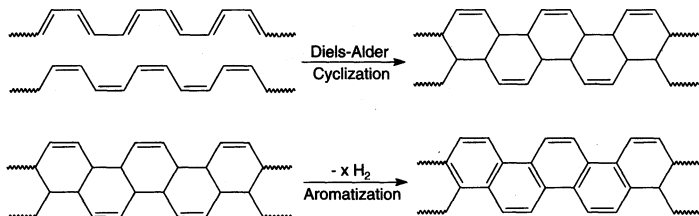


Figure 4.8 Cyclization and aromatization of PVC

olefin can either cyclize and fragment to give benzene or it can cross-link. The cross-linked material, in the same way, can cyclize and fragment to give substituted benzenes, or it can form a char.

It is believed that the mixed *cis,trans*-polyene gives rise to aromatics and smoke, whereas if isomerization occurs to an all-*trans* form, cross-linking and hence char formation will occur. This isomerization is apparently promoted by Lewis acids; the most common materials in use for PVC smoke suppression are molybdenum salts which promote the isomerization [95–97]. A recent publication focuses on a new mechanism for the cross-linking of PVC, reductive coupling [98]. Low valent metal salts, usually Cu(I), promote gel formation and reduce the evolution of hydrogen chloride. PVC is inherently flame retardant owing to its very high chlorine content; the oxygen index has been measured at between 45 and 49 [99].

The degradation of poly(vinylidene chloride) has recently been reviewed by Šimon [100] and Howell [101]. The degradation occurs in two stages, with the first stage completed by 220°C. The major product is HCl but there is also a small amount of monomer produced. The presence of chlorine permits the loss of HCl by chain-stripping while the presence of disubstituted carbons means that end-chain scission, and hence monomer formation, can occur. This first step leads to the formation of conjugated double bonds, just as in PVC, but there is no apparent autocatalysis for this polymer. The polychloroacetylene units that are produced give rise to color, and even at 1% degradation the polymer is insoluble. The second step of the degradation involves some cross-linking, probably by a Diels-Alder pathway, to give a large surface area, highly absorbent form of carbon.

Stabilization of poly(vinylidene dichloride) can occur by several means [102]. Howell et al. have studied the effects of metal formates on the degradation of vinylidene chloride copolymers [103]. Some salts have little effect while others can markedly decrease the rate of both initiation and of propagation of the degradation. This seems to depend on the ability of the metal ion to interact with chlorine. The presence of some comonomer with the vinylidene chloride can enhance thermal stability. This interrupts the conjugation that is formed by HCl loss and enhances the utility of the polymer. The presence of groups that can consume evolved HCl may be beneficial. Uhl [104] has examined the effect of magnesium hydroxide

on the degradation and concluded that it does not enhance the thermal stability of the polymer.

Polytetrafluoroethylene (PTFE). The thermal degradation of PTFE has recently been examined by Simon and Kaminsky [105], who have reviewed the extensive literature on this topic. Because of the high strength of the carbon-fluorine bond, it is not easily cleaved and reaction occurs solely by breaking of carbon-carbon bonds. In this regard it may be considered to fall into the classic pattern noted earlier, because the carbon is disubstituted, one would expect that end-chain scission would occur with the formation of monomer. Indeed up to 97% monomer is observed when the degradation is performed in a vacuum. The yield drops significantly at higher pressures and products such as hexafluoropropene, perfluorocyclobutane, and other fluorocarbons are formed. These are considered to arise from secondary reactions from the principal products of the degradation, tetrafluoroethylene and difluorocarbene. Both of these primary products arise from simple carbon-carbon bond cleavage. Some of these secondary reactions are shown in Fig. 4.9.

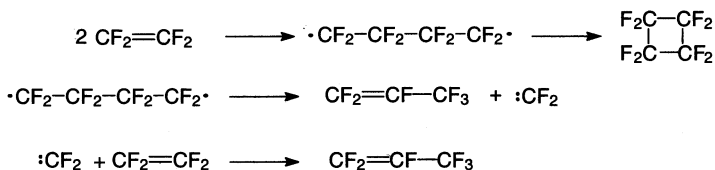


Figure 4.9 Secondary reactions of tetrafluoroethylene to form observed degradation products

Polyamides. The thermal degradation of polyamides has been studied using pyrolysis-gas chromatography [106], infrared spectroscopy of condensates [107, 108], and mass spectroscopy [109, 110]. The products of the degradation of aliphatic polyamides consist of several components. The types of products that are formed and their relative amounts depend on the particular type of polyamide that is studied. For polyamide 6, the major product of the degradation is caprolactam. This is formed by cleavage of the relatively weak C-N bond followed by cyclization as shown in Fig. 4.10.

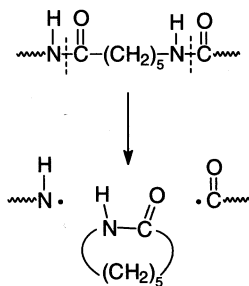


Figure 4.10 Formation of caprolactam from the degradation of polyamide 6

For larger polyamides, the lactam product is much less important, probably because of the reduced chance of ring formation with the longer chain. The major products are now mononitriles and -olefins have been observed in some cases. A scheme to account for these products has been suggested and is shown in Fig. 4.11. In addition to the products mentioned earlier, hydrocarbons are also noted among the products. These include alkanes, α -olefins, and α , ω -diolefins, with the olefins being the major component. These are also observed for those polyamides formed from diacids and diamines.

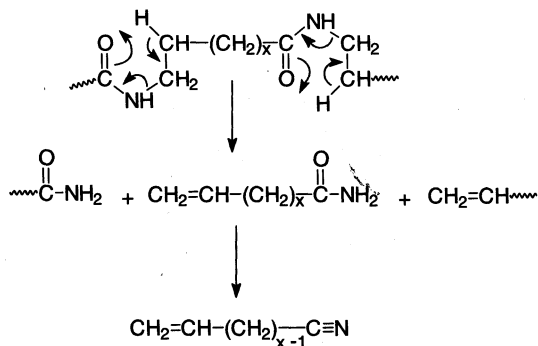


Figure 4.11 Formation of mononitriles from the degradation of polyamides

The major product observed in the degradation of polyamide 6,6 is cyclopentanone. This is formed by cleavage of the two C-N bonds to give a diradical at the two carbonyl centers. This can then rearrange to give cyclopentanone and carbon monoxide. A small dinitrile peak is also observed and this is more important in larger polyamides. This is believed to be due to a pathway similar to that shown previously for the mononitrile. When the polyamide is prepared from a diacid and a diamine, two amide end groups can be formed, in contrast to only one when a half-acid, half-amine compound is used. Figure 4.12 leads to the formation of the diolefin as well as the dinitrile via a -hydrogen shift.

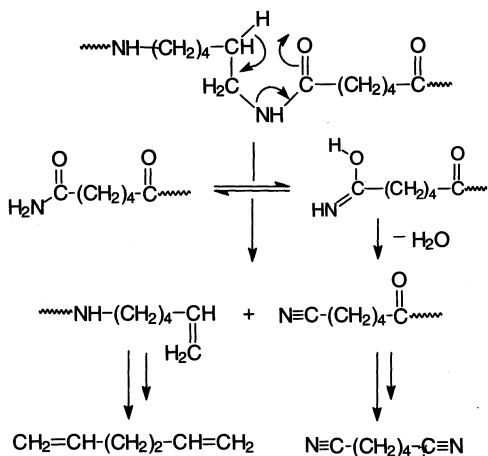


Figure 4.12 Formation of 1,5-hexadiene and 1,4-dicyanobutane from polyamide 6,6

Levchik et al. [111–116] studied the thermal degradation of various polyamides in the presence of ammonium polyphosphate and other inorganic phosphorus compounds. The presence of ammonium polyphosphate changes the degradation process by lowering the temperature of decomposition and changing the composition of the volatile products. This is an intumescent process in which the volatile products that are produced from the decomposition of the polyamide can blow the layer of polyphosphoric acid that is mixed with the residue of the degradation. Wheeler, Zhang, and Tebby [117] have described the utilization of organic phosphates to enhance the thermal stability of polyamides. Mateva [118] has reported that a

flammability and thermal behavior of polyamide 6 is changed when the polymerization of caprolactam is carried out in the presence of some N-substituted phosphorus-containing lactams.

Polyamide 6 has been irradiated both in the presence and absence of flame retardants and radiation promoters [119]. The gel content and cross-link density are increased in the presence of a radiation promoter, such as melamine cyanurate. Invariably the onset temperature of the degradation is decreased after irradiation. Polyamide nanocomposites show a reduction of 30 % or more in the peak heat release rate [23, 24].

Polyesters. The degradation of poly(ethylene terephthalate) (PET) has been studied most extensively and only that material is covered herein. It is believed that the initial step in the degradation of PET involves a typical ester degradation as shown in Fig. 4.13 [120–126].

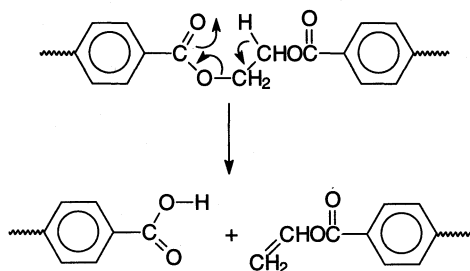


Figure 4.13 Degradation of PET to a carboxylic acid and a vinyl ester

These initial products can then undergo secondary reactions to produce the final, volatile products of the degradation; a pathway to these products is shown in Fig. 4.14.

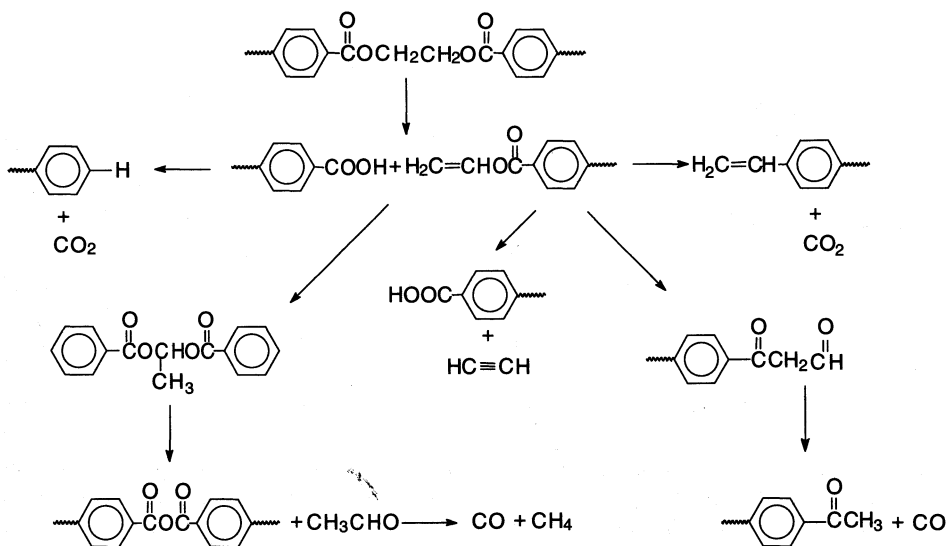


Figure 4.14 Thermal decomposition pathway for PET that gives rise to the observed volatile products

Chang [126] has suggested a four-step pathway by which the thermal stability of PET may be enhanced. The initial step makes use of the known initial step of the degradation reaction, that is, the ester decomposition reaction to give a carboxylic acid and a vinyl ester. Homopolymerization of the vinyl ester, followed by chain-stripping with the loss of a substituted carboxylic acid, will produce unsaturation along the main chain of the polymer. These unsaturated linkages can then cyclize to give a highly cross-linked and aromatic polymer.

Flame retardancy of PET is usually achieved by vapor phase processes using halogen or phosphorus compounds.

Polycarbonates. The first article on the degradation of polycarbonates appeared in the early 1960s and it has continued to be an active area of investigation up to this time [127–144]. In this review attention is devoted only to bisphenol A polycarbonate. The major gaseous product evolved in the thermal degradation is carbon dioxide, which is taken to indicate that the carbonate linkages are easily cleaved. Additional gaseous products are carbon monoxide and methane, and these increase in abundance as the temperature is raised. Phenols are also evolved. It is believed that cyclic oligomers are the primary products of polycarbonate degradation, but there is controversy about whether this proceeds by an ionic or a radical process. Figure 4.15 shows the radical pathway, after McNeill [138], for the formation of the cyclic oligomers as well as phenol. The radical scheme is used here for convenience; this should not be taken as a preference for this pathway.

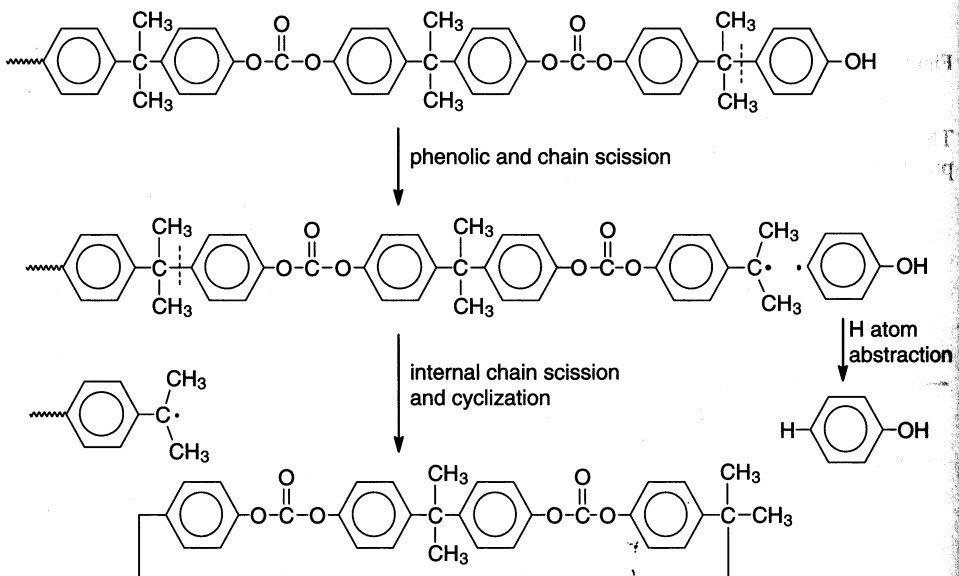


Figure 4.15 Radical pathway for the formation of cyclic oligomers from bisphenol A polycarbonate

Polycarbonates undergo extensive gel formation when heated in an open vessel or under vacuum but not when heated in a sealed tube. The cross-linking reaction proceeds with the formation of diaryl ester, ether, and carbonaceous bridges.

The flame retardants that have been used for polycarbonate include brominated phosphates [145–147], zinc borate [148], aromatic sulfonates (intumescent) [149], and resorcinol bis(diphenyl)phosphate [144, 150]. All, except the intumescent system, function in the gas phase as radical traps.

4.2.1.4 Concluding Comments

In this section we have attempted to delineate the various pathways by which thermoplastics may undergo thermal degradation as well as to give some indication of the types of investigations one may use to develop this type of information. In addition, information is provided on processes, which can be used to change the degradation pathway and render the polymer less flammable. We hope that the reader will be able to use this as a guide to the literature. We have not attempted to cover every article on any of the polymers, rather we have tried to give a sampling of the work which has been already accomplished and the new worker in this area is invited to build on this work so that a better understanding of the thermal degradation of polymers, and the means to prevent this degradation, can be developed.

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