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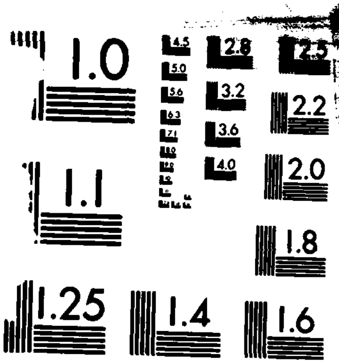
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Research was conducted on high char forming polymers systems. Work has established two principles for high char formation at elevated temperatures:- 1. the formation of thermally stable crosslinks and 2. the formation of thermally stable ring structures. This research has dealt primarily with the latter and a large part of it has concentrated on substituted aramids.

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Eli M. Pearce
2/25/86

Abstract

This is a review through 1985 of the research conducted at the Polytechnic University on high char forming polymer systems under Army Research Office sponsorship. Work by this group has established two principles for high char formation at elevated temperatures - 1. the formation of thermally stable crosslinks and 2. the formation of thermally stable ring structures. This research has dealt primarily with the latter and a large part of it has concentrated on substituted aramids.

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MECHANISMS OF CHAR FORMATION DURING FLAMMABILITY

1. INTRODUCTION

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Considerable interest in recent years has been devoted to the study of polymers which are flame reistant. With sufficient heat and oxygen, most organic polymers will burn. Polymer flammability is related to a number of factors such as polymer composition and structure, bond strength, char yield, nature of pyrolysis products, and exposure environment.[1-4] The stronger chemical bonds and the higher char yields are usually reflected in improved flammability behavior. In addition, polymers which can produce vapor phase inhibitors such as hydrogen halides are relatively more flame resistant. Reviews of the literature have indicated that the most flame resistant polymers usually contain wholly aromatic structures such as aromatic polyamides or polymers with multiple bonded structures, such as heterocyclic polymers with fused heterocyclic rings.[1,2,5,6]

Methods predicting polymer flammability in terms of oxygen index have a number of limitations. For example, Johnson[7] and Van Krevelen[6] have proposed a linear correlation between percent oxygen index (OI) and percent char yield. The predicted results based on these methods have been usually correct for polymers containing just C, H, and O. However, for polymers containing other heteroatoms such as halogen these relationships do not hold.[6] Difficulties in establishing a general method for predicting the oxegen index and char formation for all polymers, have made it necessary to individually investigate important new classes of polymers in order to better understand the correlation or lack of correlation that exists with polymer structure.

A series of publications from this laboratory by Pearce and co-workers have dealt with the relationships between polymer structure, char formation and flammability.[8-11] For example, in studies on a number of new epoxy resins, it was found that the diglycidyl ether of bis-phenol fluorenone showed high thermal stability but based on copolymers with the diglycidyl ether of bis-phenol acetone, there was no linear relationship between char yield and fluorene content.[11] In fact, synergism has occurred whereby the char yield has increased rapidly at low fluorene concentrations and has reached a maximum value at about 20-40% fluorene group concentration.[11] The generalized effect of such fluorene groups on improving the thermal stability of epoxy resins was previously shown by Korshak et al.[12] and has also been reported for other polymers such as polyquinolines[13] and polyamides[14] whereas the copolymer synergism had not been previously reported.

Our investigations on various phenolphthalein-related polymers[15,16] have show that polycarbonates and polyamides usually give higher oxygen indices than the corresponding polyesters of similar structure. This has indicated that the nature of the pyrolysis products have a measurable effect on the flammability of a specific polymer. Among the possible factors to consider were that polycarbonates could release more CO_2 from the breakdown of the carbonate group and polyamides could produce relatively nonflammable nitrogen-containing products during pyrolysis. The importance of the formation of high temperature stable crosslinks with that of char formation was also demonstrated by the opening of the phenolphthalein lactide ring to give intermolecular ester crosslindings.[16] In other studies, Pearce et al.[17] have attempted to provide information about the structural relationship of halogen containing phenol-formaldehyde oligomers to the flammability of the crosslinked resins. It was found, as expected, that chlorinated and brominated novolacs and resols give higher oxygen indices. The effect of various substituents on aromatic polyamides was evaluated and enhanced char formation was noted for certain chlorine containing aramids, in part because of benzoxazole formation.[18-22]

A number of polymers containing heterocyclic structures incorporated in the polymer chain such as benzoxazole, benzimideazole and imide have been shown to confer a high order of flame resistance and thermal stability.5,23-26

Some of the studies[15,17] as well as that of others[23-2] have shown that in many cases structural modifications of polymers leading to increased flame resistance have involved the deterioration of their original thermal stability, e.g., according to Wright et al.[23] the presence of flame retardant halogen substituents in an aromatic ring of polyphenylenes reduces stability by an amount dependent upon the degree of substitution, type of polymer and type of halogen.

2. Wholly Aromatic Polyamides

Wholly aromatic polyamides like poly(1,3-phenyleneisophthalamide) and poly(1,4-phenyleneterephthalamide) are well known for their improved resistance to flammability. Utilization if this characteristic has been made in uniforms, carpets, aircraft interiors, etc. Modification to further decrease the flammability of these materials has obvious importance.

A number of articles on the thermal stability of aromatic polyamides have appeared in the literature wherein the results of thermal degradation studies have not been consistsistent19,29,17-30,31 and little information has been available on the correlation between thermal stability and flammability.

Krasnov et al.27,28 investigated the pyrolysis of poly-(1,3-phenyleneisophthalamide) and poly(1,4-phenyleneterephthalamide) and found that similar volatile products were formed during the pyrolysis of each polymer. Carbon dioxide, water, carbon monoxide, benzene, hydrogen cyanide, toluene, benzonitrile, hydrogen and ammonia were produced as the major products during pyrolysis, and the quantity of each of the products was related to the pyrolysis temperature. The authors suggested that hydrolytic degradation reactions occurred during the pyrolysis. This suggestion was supported by Chatfield et al.[31] on the basis of his thermal degradation study of poly(1,3-phenyleneisophthalamide).

Ehlers et al.[29] and Friedman et al.[30] have reported that during the pyrolysis of aromatic polyamides almost no free water was formed, which implied that hydrolytic reactions were improbable and the authors suggested the possibility of carbodimide formation during the thermal decomposition of aromatic polyamides.

In our studies[19-21] related to the flammability and thermal behavior of poly(1,3-phenyleneisophthalamide) and poly(1,3-phenyleneisophthalamide) and poly(1,4-phenyleneterephthalamide), we found that the thermal decomposition of these aromatic polyamides involved both homolytic as well as hydrolytic cleavages of the amide units. At lower temperatures homolytic reactions became increasingly important. The homolytic cleavages appeared to involve all the nonaromatic ring bonds. These polyamides have given high char yields (about 60% at 700°C) and good flame resistance (oxygen indices above 30) as reported in several other papers.[5,6,23,24]

3. Halogenated Aromatic Polyamides

Systematic attemps to correlate halogen substituent effects on thermal and flammability properties of aromatic polyamides were not previously reported, and in particular, there was no available information on the synthesis and thermal properties of the bromo-substituted aromatic polyamides.

Pearce et al.[18,19-21] have reported on the modification of aromatic polyamides with regard to their thermal stability and flammability by the incorporation of various substituents into the polymer backbone. It was found that high char yields and flame resistance were associated with polymers having a chlorine substituent. Pyrolysate analysis with Gas Chromatography-Mass Spectrometry suggested that during the thermal degradation of chlorinated aromatic polyamides, cyclic structures were formed.[21] Chatfield et al.[32] also had studied the thermal behavior of a post-chlorinated poly(1,3-phenyl-isophthal- amide), but this was a fabric sample with unknown structure in regard to chlorine substitution. Thus, on the basis of HPLC chromatograms for the high-boiling volatiles and the infrared spectra of the solid pyrolysate residue, these authors were not able to draw convincing conclusions concerning the thermal degradation mechanisms of this "chlorinated" aromatic polyamide. Diaz et al.[33] had investigated the chlorinated aromatic polyamides derived from perchloroterphthaloyl chloride, but did not report sufficient information in regard to either thermal stability or flammability.

The thermal stability of fluorine containing poly(2,3-phenylene-isophthalamides) were investigated by Shungo et al.[34] The authors have reported that introduction of fluorine into the diamine aromatic ring enhanced heat resistance as compared to the corresponding unsubstituted polyamide, while introducing fluorine into the isophthaloyl aromatic ring had the opposite effect. Malichenko et al.[35-37] found that aromatic polyamides which were prepared from a fluorinated polyphenylene diacid chloride or from the diamine containing fluoroalkyl groups showed higher thermal stability than the corresponding unsubstituted polyamides.

Studies by us have established mechanistic routes for the formation of benzoxazole structures upon thermal treatment for ortho-halo diamine substituted aramides. These studies were conducted on model chlorine containing diamides to better understand the mechanisms.[22,38] Kinetic studies confirming the proposed mechanisms for homolytic scission and ring formation were done on the chlorine containing aramids.[39] Pyrolysis experiments on the respective chlorine, fluorine and bromine containing aramids detected 2-phenyl-benzoxazole in the pyrolysis products.[20,40] We also studied the synthesis and thermal stability of several N-methylated, non-iminolizable, unsubstituted and chloro-substitued aramids and established that iminolization is a necessary condition for enhanced char formation in haloaramids where benzoxazole formation can occur.[41]

Our studies on the thermal and flammability property differences between poly(1,4-phenylene terephthalamides) derived from 2-mono- or di-2,5-halogenated 1,4 phenylediamines, where halogen is bromine, chlorine, and fluorine, established the influence of homolytic scission as primary for oxygen index improvement (Br>Cl>F) and benzoxazole formation for increased char formation (F>Cl>Br).[42,43] During the course of these studies we also looked at the effect of meta or para linkage and the presence of halogen substituents on thermal stability. It was found that polyamides containing para units are more thermally stable than those containing meta units for both halo-substituted and unsubstituted aramids.[43,47] Low molecular weight model compounds for investigating the relationship between the formation of benzoxazole from halogenated amides and the existence of the iminol forms of the amides were studied.[45] For example, 2-fluorophenyl isophthalamide showed the iminol form melting at 180°C and the amide form melting at 212°, with the tautomeric structures confirmed by infrared spectral studies. Thermal degradation of the model compounds produced benzoxazoles.

Our studies on the fluorinated aromatic polyamides confirmed our previous observations that substituting terephthaloyl units for isophthaloyl units usually increased the thermal stability of the polymer.[44,46] We therefore decided to look at the effect of other linking groups in the diamine portion of the aramid-groups such as methylene and sulfone.[46] The thermal stabilities of poly (5,5'-sulfonyl-2,2'-difluoro-diphenyl terephthalamide) and the isopthalamide analogue were close to each other. This was attributed to both the relative flexibility of the $-SO_2-$ group and also to an activating effect on the dehydrofluorination reaction. With fluorinated aromatic polyamides having ortho fluorine to the amide nitrogen, the electron releasing $-CH_2-$group deactivated the dehydrofluorination reaction and the electron withdrawing group $-SO_2-$ activated nucleophilic substitution so that the aramid from the methylene bridged difluoro-diamine was more stable than that from the difluro-m-phenylenediamine, which in turn was more stable than the sulfone bridged difluoro-diamine.

We presently have some preliminary studies comparing other fused heterocyclic structures which have indicated that (poly(2,4-difluoro-1,5-phenylene trimellitic amide-imide) is more thermally stable and gives a higher char yield than poly (2,4-difluoro-1,5-phenylene isophthalamide). In addition, there is some preliminary evidence that zinc chloride can increase the char yield from unsubstituted aramids.

4. Nitro Containing Aromatic Polyamides

More recently we have found that an ortho nitro-group on the diamine portion of the aramid may be extremely efficient as a leaving group for the formation of benzoxazole units.

Thermal decomposition of ortho substituted polyamides proceeds via a two stage mechanism, whereas unsubstituted polyamides decompose in one step (Fig. 1 & 2). The first step represents the loss of HNO_2 and the second step is due to degradation of the resulting benzoxazole polymer. Substitution of hydrogen by NO_2 results in a substantial lowering of the initial decomposition temperature (IDT).

Comparison of TGA data (Table 1) for nitro substituted and unsubstituted aromatic polyamides shows a substantial lowering of the IDT and an increase of the char yield for nitro substituted polyamides except for poly(2,4-dinitro-1,5-phenylene isophthalamide), (2,4-$DiNO_2$PMI) and poly(2,4-dinitro-1.5-phenylene terephthalamide), (2,4-$DiNO_2$ PMT) at 900°C. The increase in the char yields of nitro substituted aromatic polyamides may be attributed to the intramolecular cyclization and or intermolecular crosslinking reaction during thermal degradation in contrast to the breakdown of the main chain as the primary reaction of unsubstituted polyamides under degradation. The lower char yield of 2,4- $DiNO_2$ PMI and 2,4-$DiNO_2$ PMT must be the result of the evolution of two NO_2 groups on a phenylene unit under degradation conditions. Upon the introduction of a nitro substituent ortho to the amide group, a decrease in thermal stability is observed. A lower stability of poly(4-nitro-1,3-phenylene isophthalamide), (4-NO_2 PMI), compared to poly(1,3-phenylene isophthalamide), (PMI), may be attributed to the probable increase in chain flexibility by the nitro group; the latter can disturb the structural symmetry of the polymer segments, leading to decreased resonance effects and lower backbone rigidity. This decrease in chain stiffness probably offsets any increase caused by the steric interaction of the nitro group with the amide group. Upon the introduction of a nitro group in the diamine ring at the ortho position of poly (1,4-phenylene terephthalamide), (PPT), a drastic decrease in thermal stability is observed. Therefore, the effect of a nitro group on the thermal stability is much more detrimental in the case of PPT as compared to PMI. One of the possible explanations could be that p-phenylene linkages in PPT give rise to an extremely rigid rod-like structure and that the introduction of a substituent disturbs the structural symmetry leading to decreased resonance stabilization and a marked decrease in thermal stability. On the other hand, PMI is comparatively flexible owing to the presence of less stiff m-phenylene linkages and the presence of a substituent does not cause a dramatic decrease in the thermal stability.

Poly (4-nitro-1,3-phenylene terephthalamide), (4-NO_2 PMT) has similar thermal stability to 4-NO_2 PMI but, has a little higher char yield at 900°C. This is because

gives a much more rigid backbone than the 

and the resulting polybenzoxazole from 4-NO_2 PMT has higher heat resistance than that from 4-NO_2PMI.

Although poly(3-nitro-1,4-phenylene terephthalamide), (3-NO_2 PPT), has higher thermal stability than poly(3-nitro-1,4-phenylene isophthalamide), (3-NO_2 PPI) both polymers have similar char yields. Since both polymers undergo stable benzoxazole ring formation, the heat resistance of the resulting polymers was not much affected by the type of diacid backbone.

When the number of nitro group increases in the diamine ring at the ortho position of PMI and poly(1,3-phenylene terephthalamide), (PMT), the thermal stability decreases continuously (Fig. 3).

PMI > 4-NO_2 PMI > 2,4-DiNO_2 PMI
PMT > 4-NO_2 PMT > 2,4-DiNO_2 PMT

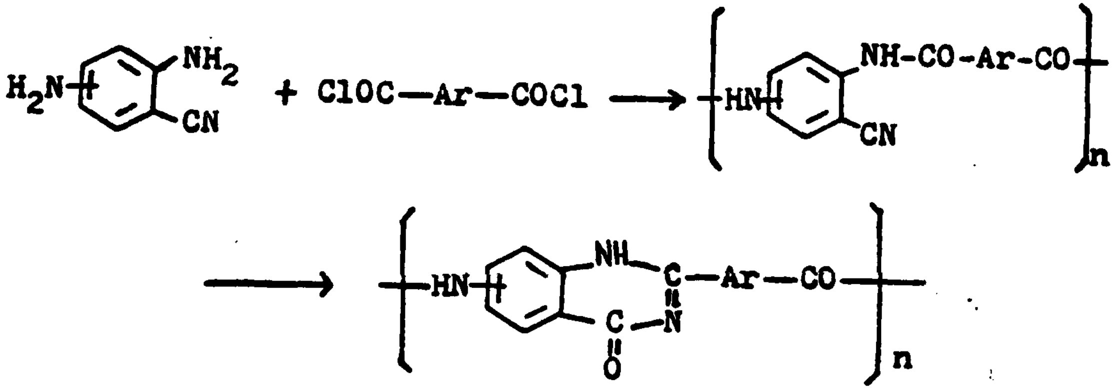
Poly(4,4'-oxydianiline terephthalamide), (PODAT), has much higher thermal stability and char yield at 900°C than poly(4,4'-oxydianiline isophthalamide), (PODAI) and when these polyamides dinitrated on 3,3' position of diamine ring there are slight differences in thermal stability and char yield. This phenomena also can be found in poly(4,4'-benzidine terephthalamide), (PBZDT), and poly(4,4'-benzidine isophthalamide), (PBZDI) (Fig. 4). This observation could be explained in terms of chain stiffness, rigidity, resonance stabilization, and steric effects as mentioned earlier.

All the mononitrated polyamides and dinitrated polyamides undergo single step intramolecular nucleophilic displacement reaction except poly(3,3'-dinitro-4,4'-oxydianiline terephthalamide), (PDNODAT) and poly(3,3'-dinitro- 4,4'-oxydianiline isophthalamide), (PDNODAI). The same phenomena was found in the case of PDNODAT and PDNODAI.

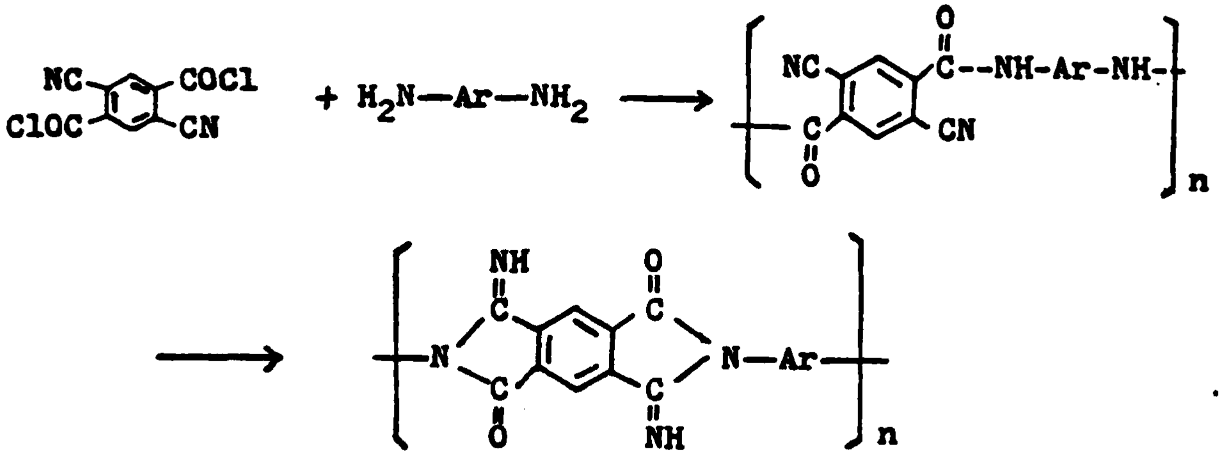
It is therefore clear that from readily available and processable ortho substituted polyamides and careful curing of polymeric materials at the IDT we can obtain poly(benzoxazoles).

5. Nitrile Containing Aramids

In recent studies, it has been found that the introduction of nitrile group into the diamine aromatic ring enhanced the heat stability of polyamides.[47-50] Barashkov et al. reported that polycyanamide prepared from 2,4- and 2,5-diaminobenzonitrile and various aromatic diacid chloride underwent isomerization cyclization resulting in polyamidoquinazolones.



Vasil'eva et al.[51] have shown that low-temperature polycondensation of 2,5-dicyano terephthaloyl chloride with aromatic diamine gave high-molecular-weight, film-forming polycyanamide. Upon thermal isomerization, it gave a new class of thermally stable polymer, the polyiminoimides which had good physicomechanical properties and high thermal stability comparable to that of polypyromellitimides.



Griffith et al.[52] showed that the addition of zinc chloride as an additive into the polymerization of N, N'-bis(3,4-dicyanophenyl) alkane diamide produced a polymer with higher thermal stability than the polymer produced without the additive.

C.S. Marvel et al.[47-49] suggested that polymer chain terminated with an aryl cyano group or aromatic units with nitrile group substituents undergo trimerization on heating or treatment with zinc chloride to produce triazine crosslinks resulting in higher thermal stability, similar to that also observed previously by us.[53] Some nitrile containing monomers, i.e., 2,4-diaminobenzonitrile (2,4-DABN) and 3,5-diminobenzonitrile (3,5-DABN) have been synthesized by us and characterized by infrared spectroscopy, nuclear magnetic resonance spectroscopy, differential scanning calorimetry, and mass spectrometry. Several nitrile-group-containing aromatic polymides were also synthesized and characterized by DSC (differencial scanning calorimeter) and TGA (Thermogravimetric Analysis). Our preliminary studies have shown that the nitrile group substituted aromatic polyamides usually gave lower thermal stability and lower crystallinity, but gave higher solubility in dimethylacetamide and N-methyl pyrrolidone and higher char yield when compared to unsubstituted, aromatic polyamides. Char yield increased with increasing cyanodiamine composition in aramid copolymers.

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