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Adventures In Fire Retardancy

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The work of the author's research group on fire retardancy over the past twenty years is reviewed.

The burning of polymers involves several steps, beginning with the cleavage of chemical bonds to give molecules with some volatility and their escape into the vapor phase. Further degradation of these species then occurs to give small radicals which actually make up the flame. Finally, the feedback of energy from the flame to the surface of the polymer continues the process (1). Fire retardants may function by interfering with any of these three steps. A retardant which functions in the condensed phase may either interfere with the degradation or prevent the feedback of energy, while a vapor-phase retardant removes the radicals which make up the flame and thus leads to an extinguishment of the fire. The typical vapor-phase fire retardant is a halogen-containing compound which thermally degrades to give halogen atoms. These will abstract hydrogen from the polymer, or from some other hydrogen source, to give hydrogen halide, which is the effective fire retardant.

During the past twenty years, my research group has been involved with many different areas of fire retardancy studies involving condensed-phase processes. We have intentionally chosen to work on condensed-phase processes because we have felt that the science would be of more interest than vapor-phase radical chemistry. The unifying theme of almost all of this work has been cross-linking and

char formation. At this time, I wish to review these areas and show the comparisons and the conclusions which we have drawn from each area of study, We have been involved with four distinct areas: 1) the effect of additives on the thermal degradation of poly(methyl methacrylate) and poly(ethylene terephthalate), 2) the use of graft copolymerization to enhance the fire retardancy of materials, 3) Friedel-Crafts chemistry to enhance the thermal stability and fire retardancy of polystyrene, and 4) the relationship between cross-linking and thermal stability.

DEGRADATION OF POLY(METHYL METHACRYLATE)

It has been well-established that poly(methyl methacrylate) (PMMA) degrades by end chain scission, also known as unzipping, to give predominantly monomer. If one considers the initial cleavage reaction, a primary radical as well as a tertiary radical are produced. It is easy to understand that the tertiary radical will unzip, but the primary radical should abstract hydrogen, and oligomers, not monomer, would be the expected product. Both Manring (2-6) and Kashiwagi (7-13) have examined this problem, and both have concluded that side chain scission also occurs. Manring (5) suggests that side chain cleavage occurs first, followed by main chain cleavage, while Kashiwagi (13) claims the opposite order for the reaction.

When we began our work on the effect of additives on the degradation of PMMA, we hoped to be able to design additives that would participate in particular reactions. At the beginning of our work, we attempted to identify the locus of reaction on both the polymer and the additive and to use that information in order to identify a new additive which might react in a similar but more efficacious manner. For instance, in the reaction of red phosphorus with PMMA, we postulated that phosphorus interacted with the carboxyl group of an MMA unit, and that elimination of methyl, methoxy phosphonium ions occurred with the concomitant formation of an anhydride (14, 15). Thus we identified occurrence of this reaction at the carboxyl functionality of the polymer and, accordingly, looked for other substances which could react at this moiety. Perusal of the literature showed that Wilkins on's salt, $(\text{Ph}_3\text{P})_3\text{RhCl}$, undergoes a reaction with an acyl halide to remove the carbonyl group and give an alkyl halide with formation of a carbonylated rhodium (16).

When a mixture of $(\text{Ph}_3\text{P})_3\text{RhCl}$ and PMMA (1: 1 by mass) was heated at 200°C for 2 hours, it was found that a cross-linked polymer was produced, as well as several products which contained rhodium and organic fragments which could only have come from the PMMA. Analysis of all of these materials showed that both intra- and inter-molecular anhydride cross-links were obtained. The starting material is obviously not useful as an additive for PMMA because of its price, color (red), and the potential toxicity of rhodium compounds. Nonetheless, these experiments showed that the premise on which we were operating was valid and that it was possible to take the results of one investigation and use them to plan the next experiment (17,18).

Since rhodium in Wilkinson's salt is a Lewis acid, it is likely that the initial reaction is coordination between the salt and the Lewis base moiety of the polymer, i.e., the carbonyl group. Any transition metal salt has the potential to function as a Lewis acid and thus coordinate to the carbonyl. McNeill had already shown that such coordination occurred and that, typically, methyl halide was eliminated if a metal halide were used (19, 20). We examined the chlorides of manganese(II), copper(I), copper(II), iron(I), iron(II), iron(III), nickel(II), and chromium(III). The degradation of the polymer is only affected

when coordination between the metal ion and the polymer occurs; there is a good correlation between the Lewis acidity of the metal ion and the effect on thermal stability. Of the ions studied, the weakest Lewis acid is Cu(I), and there is no effect on the degradation in its presence. For all other species, the degradation is affected. In some cases methyl chloride is eliminated, while in others it is absent. The appearance of methyl chloride depends upon the metal halide bond strength. When the bond strength is high, as in nickel(II) and copper(II), the halide ion is not released from the metal, and no methyl chloride is formed. On the other hand, for all other metal chlorides (except CrCl₃, discussed below) methyl chloride is released, and a metal carboxylate is produced. This metal carboxylate exists in an ionomeric form, and this stabilizes the polymer so that a significant fraction is not volatile at 600 deg C (21, 22).

The case of CrCl₃ is quite unique (23). The degradation is certainly affected by the presence of the salt; yet methyl chloride is not evolved. Rather, HCl is formed. This result was baffling for some time until we discovered that CrCl₃ undergoes a thermal reduction into CrCl₂ with the elimination of a chlorine atom. This chlorine atom is able to abstract hydrogen, and this process leads to the observed products.

Related work has been carried out by using a variety of organotin chlorides, Ph_xSnCl_{4-x}. Tin(IV) chloride behaves as a typical Lewis acid, and the first step involves coordination. When there is a phenyl group attached to the tin, the degradation of PMMA is changed completely relative to that in the presence of SnCl₄. A homolytic cleavage of the tin-phenyl bond occurs easily, and the presence of the phenyl radicals effectively prevents PMMA degradation by interacting with the MMA radicals and terminating the degradation (24 25). A similar degradation pathway has been observed for blends of PMMA with Nafion-H(R) (26) and diphenyl disulfide (27).

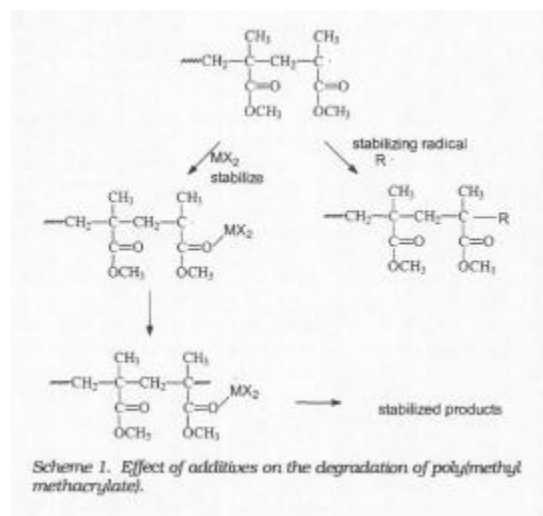
This work has demonstrated two different means by which an additive can interact and prevent the degradation of PMMA, a coordination to the carbonyl and a capping reaction. These are both illustrated in Scheme 1.

Work on poly(ethylene terephthalate) (PET) has been much less extensive but has had the same goal of understanding the locus of reaction on the polymer and then designing an additive to interact at that site. The original work involved the interaction of red phosphorus with PET (28). This investigation showed that phosphorus did affect the degradation of PET and that cross-linking appeared to occur. In later work (29), it was proposed that Friedel-Crafts alkylation of PET occurs; the cleavage of the ester bond gives a carboxylic acid and a vinyl ester, and the vinyl group then serves as the alkylating agent. This suggested mechanism is no longer considered viable in this research group and has been replaced by another pathway (30). The new pathway for PET stabilization involves a series of four reactions: ester cleavage to give a vinyl ester and a carboxylic acid, vinyl polymerization to give a new polymer, chain stripping to give an unsaturated species, and cyclization to give aromatic compounds or, at least, compounds which can easily aromatize. This overall pathway is shown as Scheme 2.

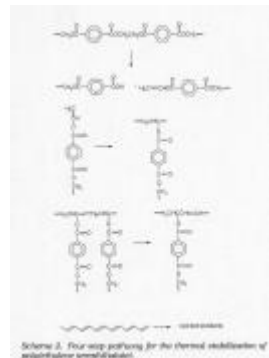
GRAFT COPOLYMERIZATION TO ENHANCE FIRE RETARDANCY

The focus of the majority of the work of this laboratory has been on cross-linking and char formation to enhance the thermal stability of polymers. If one can attach, by any process, a char-forming material to the surface of a polymer, and if that char-former degrades and protects the surface of the polymer, one may be able to enhance the thermal stability and hence, improve the fire retardance of polymers.

The premise of this work is that char that is formed on the surface of a polymer will insulate the underlying polymer from the heat source and make the thermal degradation more difficult. The advantages of char formation in order to enhance thermal stability have been reviewed and will appear in a forthcoming book (31). Another motivation in this work is the realization that every polymer is different and may require a different strategy to achieve thermal stabilization. For instance, the degradation of poly(methyl methacrylate) is quite different from that of poly(ethyl methacrylate), while polystyrene degrades differently from polymethylstyrene. If one could develop a general procedure which would promote char formation on a variety of polymers, this development could greatly enhance the ability of the fire-retardant community to design additives to enhance thermal stability.



Scheme 1. Effect of additives on the degradation of poly(methylmethacrylate).



Scheme 2. Four-step pathway for the thermal stabilization of poly(ethylene terephthalate).

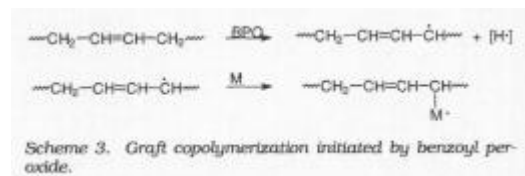
The requirements are to identify suitable char-forming monomers and processes to deliver these monomers to the surface of the polymer to be protected. The classic char-former is a material which will degrade to produce graphite and/or amorphous carbon; the notable example of this type of polymer is polyacrylonitrile (32). A second class of potential char-formers consists of materials which may degrade to produce an inorganic salt such as sodium carbonate, sodium sulfate, etc. investigations on the thermal degradation of polymers have identified some of these polymers, and from this information, one can identify other likely systems. The work of McNeill et al. (33-36) on salts of acrylic and methacrylic acid has shown that these salts degrade to produce the carbonates along with a small

amount of elemental carbon. In some cases, e.g., calcium carbonate, the salt is thermally unstable and loses carbon dioxide to give the metal oxide. In the case of poly(sodium methacrylate), 50-60% of the polymer is converted into residue which is nonvolatile at 600 deg C. From this laboratory has come work on poly(sodium styrenesulfonate) (37). This polymer degrades to produce sodium sulfate and sulfite along with some carbonaceous material. One can generalize on these two possibilities and suggest that polymers which contain an anion that is attached to both a polymer and a metal may have potential for this usage.

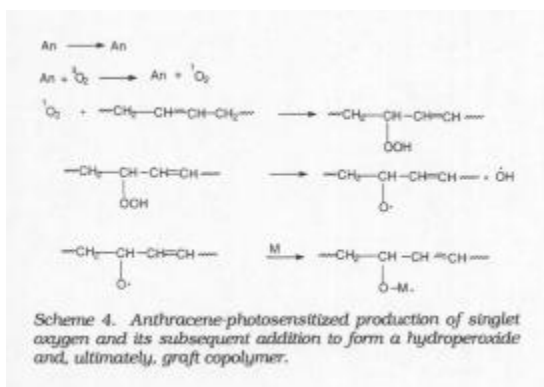
The second problem is the delivery of the char-- former to the polymer. This can be either a physical process, Le., blending, or a chemical process, copolymerization. If delivery to the surface is desired, blending is unlikely to be an option. However, one must remember that migration of the degrading material could occur and that this process could deliver the char-former to the surface of the polymer. Graft copolymerization onto a polymer is likely to be a useful means to deliver the polymer to the surface, but regardless of the process which is used, the possibility of migration of the degrading polymer must be considered.

The initial work from these laboratories focused on graft copolymerization onto a solid piece of polymer. In that work the desired char-former used was sodium methacrylate. Unfortunately, we still have not found procedures which would enable graft copolymerization of sodium methacrylate directly onto a polymer. Rather, it has been necessary to graft copolymerize the acid and then convert that into the salt. In this section, I will discuss graft copolymerization of methacrylic acid and acrylic acid onto acrylonitrile-butadiene-styrene terpolymer (ABS) and styrene-butadiene block copolymers. There are two types of styrene-butadiene block copolymer, a butadiene-rich material, supplied by Shell Chemical Company and known as SBS, and a styrene-rich material, supplied by Phillips Petroleum and known as K-resin.

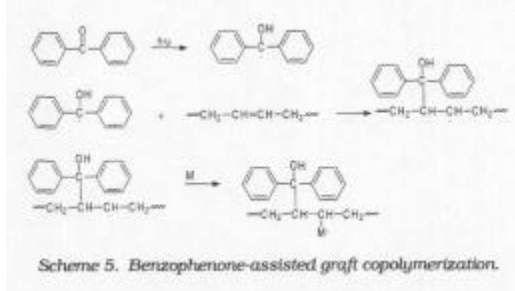
Graft copolymerization of a monomer onto a butadiene-containing copolymer may be accomplished by a variety of techniques. The standard process would utilize an initiator such as benzoyl peroxide (BPO) to remove a hydrogen atom from the polymer chain and form a radical site; this radical site is then used to initiate graft copolymerization. The general process is illustrated in Scheme 3 (38). It should be noted that homopolymerization can and does occur along with the formation of the graft copolymer.



Scheme 3. Graft copolymerization initiated by benzoyl peroxide.



Scheme 4. Anthracene-photosensitized production of singlet oxygen and its subsequent addition to form a hydroperoxide and, ultimately, graft copolymer.



Scheme 5. Benzophenone-assisted graft copolymerization.

Table 1. Thermogravimetric Analysis of ABS onto Which (Meth)acrylate Had Been Graft Copolymerized.

Sample	Actual Residue, %	Calculated Residue, %
ABS- <i>g</i> -AA, 48%	8	6
ABS- <i>g</i> -NaAA, 10%	15	8
ABS- <i>g</i> -NaAA, 32%	24	16
ABS- <i>g</i> -MAA, 10%	7	5
ABS- <i>g</i> -NaMAA, 10%	6	5
ABS- <i>g</i> -NaMAA, 20%	15	6

A second process utilizes the anthracene-photo-- sensitized production of singlet oxygen; this adds at an allylic position in the butadiene block to give a hydroperoxide, and this is then thermally cleaved. This process is shown in Scheme 4 (39).

The third procedure utilizes benzophenone as a photoinitiator (40); this method is shown in Scheme 5.

Graft copolymerization onto ABS has been carried out in this laboratory by using all three procedures (41-43). More homopolymer is produced with benzophenone than with anthracene, and there is an apparent interaction between the monomer and the initiator. Anthracene is more efficient for methacrylic acid, while benzophenone gives high graft yields for acrylamide. There is a substantial difference in the extent of graft copolymerization for acrylic acid and methacrylic acid, and this difference appears to be related to the solubility difference between these two compounds in ABS. When the graft copolymerization was performed by using chemical initiation (BPO as initiator), the extent of copolymerization of acrylic acid was much higher than for a photosensitized route (43).

Thermogravimetric analysis of samples in which the acid was converted into its sodium salt, by treatment with sodium hydroxide, revealed that a significant fraction of the ABS did not volatilize from ABS graft poly(sodium methacrylate). Knowing the amount of sodium methacrylate which has been graft copolymerized onto the ABS, one can calculate the fraction that is not expected to volatilize. Any additional material which does not volatilize at elevated temperature is then base polymer that has been rendered nonvolatile owing to the protection which was offered by the addition of the char-former. The data for ABS to which has been grafted various amounts of different char-forming monomers are shown in Table 1.

Small changes in the amount of nonvolatile residue, such as a 1 or 2% change in the fraction which is not volatile at elevated temperatures, may be simply experimental scatter and should be ignored. Indeed, repeat experiments show a variation of 1 to 2% in the amount of char. On the other hand, a difference of 7% (for the graft copolymer of ABS with sodium acrylate) is significant and must indicate that some substantial amount of the underlying ABS has been retained. Since the free acids form only a little char, these are not efficacious in any amount. The sodium salt is effective when the amount of sodium (meth)acrylate that has been graft copolymerized is larger than about 10%. When less than 10% has been added, a continuous layer of char may not be produced, and thus the underlying polymer can escape. As the amount of (meth)acrylate salt increases, a point of diminishing returns is eventually reached. At this stage a complete film of char is formed, and additional salt does not enhance char formation.

The goal of this work is to enable the retention of polymer under fire conditions, but the TGA study described above does not, in any way, conform to fire conditions. An investigation using cone calorimetry was begun in order to assess the effectiveness under conditions which more closely approach those of a fire. In cone calorimetry a sample is combusted at a given heat flux, and the rate of heat release (HRR), as well as measurements of mass loss, smoke, etc., are performed. The heat flux which is used can be varied over a relatively broad range, corresponding to different fire scenarios. In our initial studies we have used the relatively low heat flux of 25 kW/m². The measurables will change as the heat flux is varied. Presented in Table 2 are some of the results for the cone study of ABS and ABS modified with 21% of methacrylic acid (converted into its sodium salt before measurement).

These are outstanding results, and they give great encouragement to this approach to enhancing the fire retardancy of polymers. The rate at which mass is lost is significantly lower, and there is a corresponding change in the amount of energy that is released during the combustion. It takes approximately twice as long for the sample to combust; the peak heat release rate is decreased by a factor of 3.5; and it takes twice as long to reach the peak HRR.

Table 2. Cone Calorimetric Study on ABS and ABS Modified with Methacrylate (25 kW/m²).

	Virgin ABS	Modified ABS (21% Methacrylate)
Time to ignition, s	285	460
Peak heat release rate (HAR), kW/m ²	900	260
Time to peak HRR, s	530	1130
Mass loss rate, mg/s	170	40
Total smoke, m ² after 20 min	58	29

Table 3. Thermogravimetric Analysis for Graft Copolymers.

Sample	Actual Residue, %	Calculated Residue, %
SBS- <i>g</i> -NaMAA, 10%	9	1
SBS- <i>g</i> -NaMM, 20%	14	3
PA-6- <i>g</i> -NaMAA, 115%	52	20
PS- <i>g</i> -AN, 11%	5	4
PS- <i>g</i> -AN, 25%	14	10
PS- <i>g</i> -AN, 30%	17	12

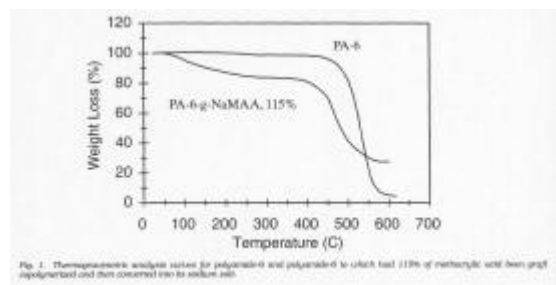


Fig. 1. Thermogravimetric analysis curves for polyamide-6 and polyamide-6 to which had 115 % of methacrylic acid been graft copolymerized and then converted into its sodium salt.

These results have encouraged even more activity in this area: studies have been performed on the graft copolymerization of methacrylate salts onto styrene--butadiene block copolymers and polyamide-6 (PA-6), and of acrylonitrile onto polystyrene, in order to verify the generality of this approach. The TGA results for these systems are shown in Table 3.

For the case of SBS, and especially for the case of polyamide-6, the actual residue is much larger than that expected, and this finding gives encouragement. In the case of SBS, the results are comparable to those obtained with ABS. It appears that the process is successful for both ABS and SBS.

The case of polyamide-6 requires additional discussion. If one views the actual TGA curve, shown in Fig. 1, for the PA-6 system, it is obvious that this curve should not be considered encouraging. In the presence of the graft layer, the onset of the degradation is at a significantly lower temperature than in virgin PA-6. This difference has been attributed to the presence of a substantial amount of the acid still present within the sample and to the well-known acid instability of PA-6. While the fraction of residue is encouraging, one cannot think of this as having enhanced thermal stability. The amount of residue that is obtained is dependent upon the temperature at which the acid is converted into its sodium salt. In Fig. 1, the sodium salt was formed at room temperature, and the amount of nonvolatile residue is about 30%. In Table 3, the entry shows that 52% of nonvolatile residue was obtained; this was from reaction at elevated temperature. This difference is likely to be simply a reflection of the extent of conversion from acid into salt.

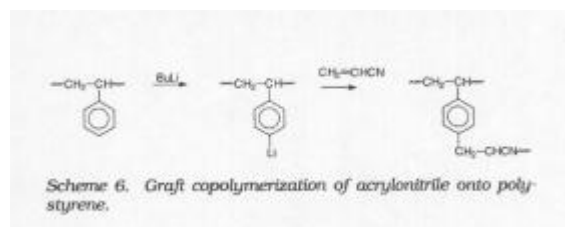
Graft copolymerization of acrylonitrile onto polystyrene requires a completely different process. We have found that it is not possible to remove the benzylic hydrogen with a radical initiator. In fact, even an alkyllithium will not form the benzylic anion but rather removes a proton from a ring position. Neither methacrylic acid nor sodium methacrylate are compatible with an alkyllithium reagent, so a

different monomer must be chosen. Since the degradation of polyacrylonitrile (PAN) is known to produce elemental carbon, we have chosen to use this as the material to be graft copolymerized onto polystyrene. A schematic view of the reaction is shown below in Scheme 6.

It should be noted that the actual residue for the poly(styrene-g-acrylonitrile) (Table 3) is only a little larger than what one expects based upon the fraction of acrylonitrile which is attached. Even so, it is larger. This result indicates that the graft layer is effective even in this system.

If this approach is to be useful in order to enhance the thermal stability of polymers, it must perform satisfactorily under fire conditions. As noted above, cone calorimetry has been used to make this assessment, and the results are shown in Table 4. Since the thermal stability of polyamide-6 is affected so adversely by the presence of the graft layer, no cone work has been carried out on this system.

Similar results have been observed when a larger amount of the graft layer is attached. These results are shown to elucidate the differences between the systems. For ABS the time to ignition is increased by 60%, while for SBS the increase is only 20%, and there is a decrease for the polystyrene graft copolymer. The peak HRR for ABS decreases by 70%, while for SBS the decrease is only 25%, and for polystyrene, 16%. All other parameters behave somewhat similarly. The cone parameters are all reproducible to 10%, so these differences are significant. It is quite puzzling that the thermal stability of ABS is substantially enhanced, while there is only a marginal improvement for SBS, related polymers, and polystyrene. The result for polystyrene may be somewhat explained by the differences in the type of char. When the graft layer consists of sodium methacrylate or sodium acrylate, an inorganic char, Na_2CO_3 , is formed which also contains a small amount of carbon. In the case of the acrylonitrile, the char layer is exclusively carbonaceous and may behave quite differently than the inorganic salt. The difference between ABS and SBS is more difficult to explain. In both cases the graft copolymer was formed by the same process, and attachment is believed to occur to the butadiene region of the polymer. It is possible that the presence of acrylonitrile leads to some polar interaction with the salt or the acid and that this enhances the retentive ability of the char. In order for this process to be successful, the char which is formed must adhere well to the base polymer and provide excellent thermal insulation. There is a large difference between methacrylate and acrylate, with methacrylate adhering much better than the acrylate. It is postulated that van der Waals interactions between the methyl group and the polymer lead to enhanced retention. This explanation implies that the composition of the polymer and of the graft layer have significant effects on thermal stability and that one must use care in the selection of both materials.



Scheme 6. Graft copolymerization of acrylonitrile onto polystyrene.

Table 4. Cone Calorimetric Results, Heat Flux=25 kW/m², for SBS and Polystyrene and Graft Copolymers of These.

	SBS	SBS-g-NaMAA, 10%	Polystyrene	Poly(styrene-g-acrylonitrile), 25%
Time to ignition, s	180	220	190	150
Peak HAR, kW/m ²	990	740	560	470
Time to PHRR, s	405	550	550	590
Mass loss rate, mg/s	183	160	141	123
Total smoke, m ² , to burnout	67	43	68	76

Based on the above information, it appears that a material which can form an inorganic char may prove to be the most useful. Three additional materials, sodium styrenesulfonate, sodium vinylsulfonate, and vinylphosphonic acid, have been investigated as potential char formers (37). The thermal degradation of poly(sodium vinylsulfonate) evolves sulfur dioxide, ethylene, carbon disulfide, and carbonyl sulfide. The solid residues contain sodium sulfate, sodium sulfite, and a graphite-like compound. When the degradation is conducted in nitrogen, 55% of the sample remains at 600 deg C and does not volatilize when the sample is heated to 1000 deg C. In air, the fraction which is nonvolatile at 800 deg C exceeds 40%. It has been postulated that the degradation proceeds by the cleavage of a carbon-sulfur bond to give an SO₃Na radical and a carbon-based radical. The SO₃Na radical can abstract hydrogen from the chain to give sodium hydrogen sulfite and a double bond along the chain. As this process is repeated, a polyacetylene is formed which will produce a graphite-like material. The NaHSO₃ will disproportionate to give sodium sulfite, sulfur dioxide, and water. A second possible fate of the SO₃Na radical is displacement on sulfur in the polymer chain with the production of sodium sulfate and SO₂.

A very similar degradation pathway is observed for poly(sodium styrenesulfonate); the polyacetylene will be styrene-substituted instead of with the hydrogen atom as in the vinylsulfonate. The nonvolatile residue in both nitrogen and air is 60% at 900 deg C.

The degradation of vinylphosphonic acid gives much less residue than that of the sulfonate salts, as might be expected due to the impossibility of salt formation from an acid. Nonetheless, the nonvolatile residue in nitrogen is 40%, with 20% remaining at the same temperature in air. Infrared analysis of the residue suggests that it is a graphitic compound containing some phosphorus oxide substitution. The degradation pathway which has been proposed is quite similar to that for poly(sodium vinylsulfonate).

Attempts failed to prepare graft copolymers of any of these materials with polymers such as polystyrene or polybutadiene, so copolymers and blends of sodium styrenesulfonate and styrene were examined (44). With graft copolymers prepared by the anthracene process, one could be somewhat certain that the graft layer was on the surface. When random copolymers and blends are formed, there is no expectation that this will be the case. Thus this approach is somewhat a test of the necessity of the graft layer residing at the surface.

Polystyrene is much less thermally stable than poly(sodium styrenesulfonate), so it is quite unlikely that the salt will be able to offer thermal protection to the styrene. If one examines the TGA curves of blends, two distinct peaks are observed, and these correspond to the fraction of each component. In the TGA of copolymers, on the other hand, there is only a single degradation step. The presence of the salt in the copolymer increases the onset temperature of the degradation by about 15 deg C but does not affect the amount of char that is formed. For the blends the onset temperature of the polystyrene

does not change when the salt is present. By the time the degradation of the polymeric salt commences, at 470 deg C, 80% of the polystyrene has degraded. When the blend contains a large amount of the salt, Le., more than about 20%, the actual amount of char that is produced is significantly larger than what is predicted based upon the composition.

If a larger sample is used than is normal for a TGA experiment, we may expect to see that degradation of the surface material occurs more easily than in the bulk and that this may afford some thermal protection. Cone calorimetry offers the opportunity to investigate this phenomenon, and the results for both blends and copolymers are shown in Table 5.

The results from cone calorimetry confirm the TGA results; blends of poly(sodium styrenesulfonate) and polystyrene are more thermally stable than polystyrene. The enhanced thermal stability must be attributed to the formation of char which occurs with the blends but does not occur with the copolymers. In a TGA/FTIR study, it was found that the copolymers do not evolve SO₂, while the blends and the homopolymer do evolve this gas. The copolymer is known to be random, and this arrangement means that there will be few, if any, adjacent sulfonate units. In the homopolymer a few routes to SO₂ were suggested, and we can now refine this proposal to suggest that SO₂ is produced by the interaction of adjacent sulfonate units. Since these are absent from the copolymer, SO₂ is not produced there, and the amount of char which is obtained is reduced and must arise from some other route.

Table 5. Cone Calorimetry, Heat Flux= 35 kW/m², for Blends of Polystyrene and Poly(sodium styrenesulfonate) and Poly(styrene-co-sodium styrenesulfonate).

	Polystyrene	Copolymer, 6% Salt	24% Blend
Time to ignition, s	45	45	40
Peak HAR, kW/m ²	795	700	290
Time to peak HAR, s	200	210	315
Mass loss rate, mg/s	198	192	84
Total smoke, m ² , to burnout	37	36	32

FRIEDEL-CRAFTS CHEMISTRY TO ENHANCE THERMAL STABILITY OF POLYSTYRENE

The work reported above has all been directed toward the formation of a char layer and the utilization of this char layer to prevent degradation of polymers. In the case of poly(methyl methacrylate), the char was to be formed via cross-linking reactions, while for graft copolymerization, the char was to be formed by the degradation of a polymeric substrate. It is difficult to enhance the thermal stability of polystyrene, and we had little success with the graft copolymerization of acrylonitrile onto this substrate as a means to enhance thermal stability. Accordingly we returned to the idea which drove all of the PMMA work, Le., identification of a functionality on the polymer which can be used as a cross-linking site and reactions at this site. In polystyrene the only functionality is the aromatic ring, so any cross-linking chemistry must involve this ring. After considering several possible reactions, we decided to do Friedel-Crafts chemistry in order to cross-link polystyrene.

The textbook example of Friedel-Crafts chemistry involves the alkylation of an aromatic ring by an alkyl halide in the presence of aluminum chloride. Obviously, if we wish to cross-link the polymer, we need a bifunctional alkylating reagent. It is equally obvious that halides are not suitable as alkylating agents, because of the evolution of hydrogen halide, and that the water and air sensitivity of AlCl_3 make this an unsuitable catalyst. After consideration of the literature, we chose to use a diol as the alkylating reagent and zeolites as catalysts. Reactivity played an important role in these choices. There can be no cross-linking during processing, or else the polymer cannot be processed; so the alkylation reaction must occur above approximately 200 deg C and preferably above 250 deg C. This requirement means that the alkylating agent must be nonvolatile at these temperatures and that the catalyst must not be effective at low temperatures. The alkylating agent of choice was "benzenedimethanol" [1,4-di(hydroxymethyl)benzene], since it is still a liquid at these temperatures.

When one combines polystyrene, benzenedimethanol, and the appropriate zeolite and heats this mixture in a sealed tube to various temperatures, one finds that cross-linking does occur, as measured by the insolubility of the product, and that the cross-linked material has enhanced thermal stability relative to virgin polystyrene (45). When the reaction was performed in an open container, the alkylating agent volatilized before it reacted. Either a more active or less volatile alkylating agent or a more active catalyst was required if this reaction were to be useful. It was decided to incorporate the alkylating agent into the polymer by preparing a copolymer of styrene with para-vinylbenzyl alcohol. The structure of this copolymer is shown below in Fig. 2: the composition ranges from 2% to 10% alcohol content.

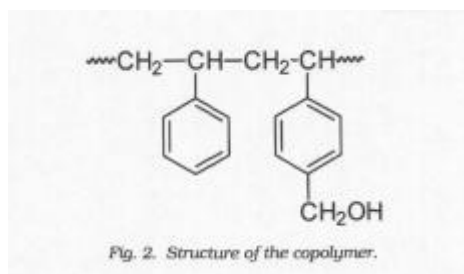
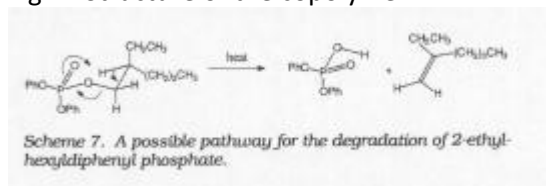


Fig. 2. Structure of the copolymer.



Scheme 7. A possible pathway for the degradation of 2-ethyl 1-hexyldiphenyl phosphate.

Table 6. Cone Calorimetry for Polystyrene, the Copolymer, and the Copolymer with the Catalyst, Heat Flux= 35 kW/m².

	Polystyrene	Copolymer	Copolymer + Catalyst
Time to ignition, s	52	37	36
Peak HRR, kW/m ²	1160	947	374
Time to peak HRR, s	162	155	410
Mass loss rate, mg/s	29	27	11

The choice of catalyst is crucial. Most potential catalysts either cause cross-linking at too low a temperature or never effect the cross-linking reaction. The material which we have found to show the most efficacious results is 2-ethylhexyldiphenyl phosphate, available commercially from Solutia as Santicizer 141 (46-48). We have found (46) that 2-ethylhexyldiphenyl phosphate decomposes at about 250 deg C to form diphenylphosphoric acid with the loss of the corresponding olefin. This reaction is shown in Scheme 7.

The unique feature of this reaction is that no catalyst is present until the thermal degradation of the phosphate ester occurs; so no cross-linking reaction may occur during processing. Depending upon the composition of the copolymer, a thermal cross-linking reaction may take place. When the copolymer contains about 18% alcohol, thermal (uncatalyzed) cross-linking occurs at 245 deg C. When the alcohol concentration is dropped to about 6%, uncatalyzed cross-linking does not occur below 300 deg C. The TGA results show that the onset temperature of the degradation, measured by the temperature at which 10% degradation occurs, increases by about 40 deg C.

This combination of ingredients has been studied by using cone calorimetry and radiative gasification (48). A radiative gasification experiment is very similar to a cone experiment, except that the gasification experiment is performed in a nitrogen atmosphere. The gasification experiment allows visual observation and study of mass and heat transfer processes during pyrolysis without the complications from gas phase combustion such as heat feedback and obscuration of the surface of the sample.

From cone calorimetry we find that the peak heat release rate is decreased by 60%. while the time to peak heat release rate is more than doubled. Some of the cone results are collected in Table 6. It is clear from these data that this combination of the copolymer and the catalyst provides a significant improvement in the thermal stability of polystyrene. The results from the radiative gasification experiment confirm these results and provide additional information on the process by which the thermal stability is enhanced. The mass loss rate for the copolymer is 2.5 times that for the copolymer with catalyst. The gasification experiment incorporates a video camera to observe the course of the reaction. For the copolymer plus catalyst, one can observe char formation in the sample cup, and this is not seen in any other case. The conclusion is that the cross-linked polymer does effectively form a char layer and that this char layer is able to insulate the polymer from the flame and prevent degradation of the polymer.

RELATIONSHIP BETWEEN CROSS-LINKING AND THERMAL STABILITY

Cross-linking to enhance the thermal stability of polymers has been a recurring theme in almost all of the work discussed above. A few years ago, in collaboration with S. Levchik, W. Schnabel, and G. Camino, we began an investigation to explore the correlation between cross-linking and thermal stability. The premise of this work was to produce a variety of cross-linked polymers, characterize the extent of cross-linking, characterize thermal stability by thermogravimetric analysis and differential scanning calorimetry, and see what relationship may exist between thermal stability and cross-linking. The characterization of the extent of cross-linking can be carried out by a measurement of the gel content and swelling ratio, i.e., Flory-Rehner theory (49, 50). The characterization of thermal stability is a more difficult problem. We have used a measurement of the fraction of nonvolatile residue as an

indication of enhanced thermal stability in much of what has been reported above. However, this is really not a measurement of thermal stability but more a measure of the fate of the early reactions which occur during thermal degradation. A more suitable measurement is the onset of the degradation, because this is truly a reflection of the first reactions which occur during the degradation. This leads to a different problem, i.e., how do you define onset? Is it the temperature at which 1% or less degradation occurs, or is it the temperature for some greater amount? We have rejected the use of a very small amount of degradation, such as 1%, owing to a concern that the cross-linking process, perhaps an irradiation process, may induce some small amount of instability in the system, and this instability would be what was measured rather than the stabilization which could also have been induced. For this reason we have chosen to use temperatures for larger values, 3% or 5% or even 10% on occasion, as the onset temperature of the degradation. Further, we examine all aspects of the degradation curve to see if other processes occur such as the formation of a primary char which is further degraded to a secondary char.

Polymeric systems which have been examined include polyamide-6 cross-linked by irradiation (51, 52); irradiated polystyrene, polybutadiene, and their copolymers (53, 54); chemical initiator cross-linked butadienes and styrene-butadiene copolymers (55); chemical initiator cross-linked polyisoprene and polychloroprene (56); and copolymers of styrene with divinylbenzene and of methyl methacrylate with various dimethacrylates (57).

Polyamide-6 has been irradiated in air and in vacuum and in the presence of various additives, some of which are flame retardants, e.g., melamine, ammonium polyphosphate, and one that has been reported to enhance the radiation-induced cross-linking, triallyl cyanurate. The gel contents are relatively constant at about 80% whether an additive is present or not, but the swelling ratio does depend on the presence of triallyl cyanurate; the cross-link density approximately doubles in the presence of the additive. The onset temperature of the degradation has been evaluated by using both 3% and 10% mass loss. There is a dramatic decrease in the temperature required to achieve 3% mass loss upon irradiation but a much smaller effect for 10% mass loss. Irradiation will lead to the cleavage of many chemical bonds, and only some of the resulting species will participate in cross-linking, while others can undergo hydrogen abstraction reactions that lead to the formation of small molecules which will easily volatilize. Therefore, 3% is considered to be too low an amount of degradation to use for the assessment of the onset of degradation.

In the presence of flame retardant additives, significant changes in the TGA curve are observed. The onset temperature of the degradation is decreased by about 100 deg C in the presence of 20% of phospham, melamine, or ammonium polyphosphate, and there is almost no dependence upon the irradiation dose. Both phospham and ammonium polyphosphate give relatively high yields of nonvolatile residue at 600 deg C, but melamine does not give appreciable amounts of char. One scheme for fire retardancy is to promote the modification of the polymer at low temperature so that the reaction scheme is changed into one which produces char and therefore offers some thermal stabilization of the polymer. This approach is somewhat contradictory, since it encourages an earlier degradation to produce materials which can form a char and then protect the polymer. Oxygen index measurements can be used to evaluate the fire retardancy of the polymer-additive combination; the oxygen index of polyamide6-melamine is higher than that of virgin polyamide-6, and this is also true of

the polyamide-6-phospham combination. However, in both cases irradiation causes a decrease in oxygen index. The presence of ammonium polyphosphate has no effect on the oxygen index, either with or without irradiation.

In the case of polyamide-6 cross-linked by irradiation, it appears that cross-linking does not enhance the thermal stability or the fire retardancy of the polymer. From infrared spectroscopy it is observed that no new bonds are formed and that, apparently, there is only some rearrangement of the atoms into somewhat different bonding patterns. That is both the original polymer and the cross-linked polymer contain C-H, C-C, C-N, etc., and no new bond types are produced. Based upon this result only, one would draw the conclusion that cross-linking does not enhance thermal stability and is not a valid strategy for fire retardancy. As will be shown below, this is not a valid conclusion.

Butadiene and its copolymers with styrene have been cross-linked both by irradiation and the use of chemical initiators, with similar results in both cases. Figure 3 shows the TGA curve for a styrene-butadiene copolymer and that copolymer which had been heated for 12 and 24 hours in the presence of dicumyl peroxide at 120 deg C in an inert atmosphere. Similar results were obtained for all butadiene-containing materials that were studied (55).

It is clear for this case that the cross-linking process does significantly affect the onset temperature of the degradation. Likewise, one can see the formation of some transitory char just below 500 deg C which does undergo degradation at higher temperatures. The formation of this transitory char is more pronounced in air, as can be seen in Fig. 4.

An investigation using X-ray photoelectron spectroscopy (XPS) was undertaken to probe the degradation further. This technique permits one to examine the char as it is formed and to probe the structure of this char. In the case of polybutadiene and related copolymers, one can observe graphitization of the polymer and thus begin to understand the process by which reaction can occur. Once again, no new bonds are formed, but there is a redistribution of the chemical bonds to produce the char structure (54).

In only one case have we seen a definite increase in the onset temperature of the degradation as the crosslinking increases, and that case is with copolymers of styrene with divinylbenzene. The TGA curves in argon and in air for copolymers of divinylbenzene and styrene, produced by using benzoyl peroxide as the initiator are shown in Figs. 5 and 6, respectively (57).

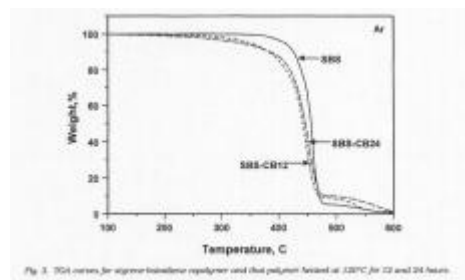


Fig. 3. TGA curves for styrene-butadiene copolymer and that polymer heated at 120°C for 12 and 24 hours.

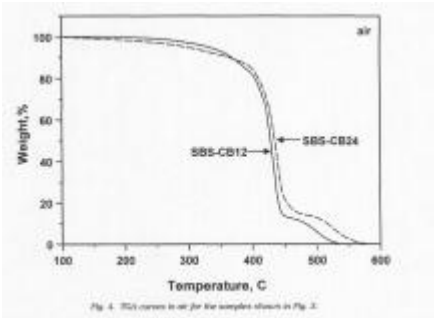


Fig. 4. TGA curves in air for the samples shown in Fig. 3.

When the thermogravimetric analysis is done in an inert atmosphere, one can see that the degradation temperature increases as the fraction of divinylbenzene increases and that more char is formed. At relatively low amounts of divinylbenzene the amount of char does not appear to change with temperature, while when the amount of divinylbenzene is high, there is an indication of a transitory char which undergoes further degradation. The same observation with respect to both onset temperature of the degradation and the amount of initial (transitory) char which is formed is also evident in air, but this transitory char undergoes complete degradation before 600 deg C is reached.

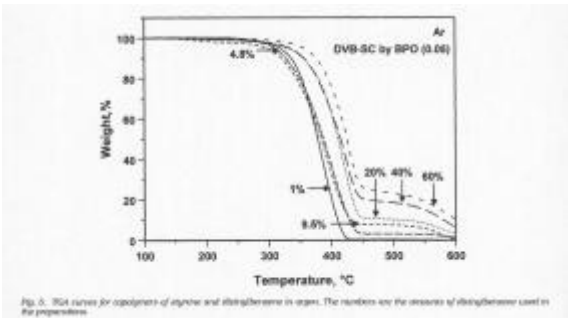


Fig. 5. TGA curves for copolymers of styrene and divinylbenzene in argon. The numbers are the amounts of divinylbenzene used in the preparations.

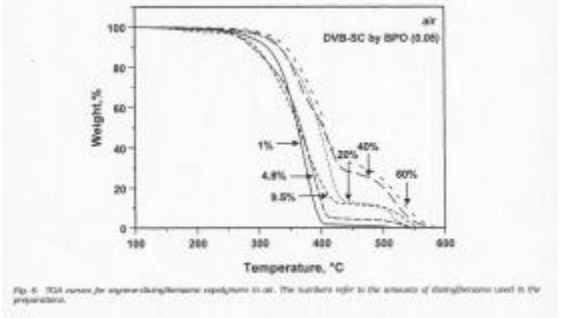


Fig. 6. TGA curves for styrene-divinylbenzene copolymers in air. The numbers refer to the amounts of divinylbenzene used in the preparations.

The behavior of the styrene-divinylbenzene copolymers may be contrasted to that of copolymers of methyl methacrylate with dimethacrylates. In Figs. 7 and 8 are shown the TGA curves for copolymers of ethylene glycol dimethacrylate-methyl methacrylate as typical of these copolymers. In argon, one sees that all of the features of the degradation are unchanged regardless of the amount of the dimethacrylate. The onset temperature of the degradation is lower for any of these copolymers than

for the homopolymer, poly(methyl methacrylate). In air the onset temperature of the degradation decreases as the amount of dimethacrylate increases.

SUMMARY

The unifying theme of all areas of research that have been addressed above is the formation of char. For poly(methyl methacrylate) it has been shown that various additives can interact with the degrading polymer, by at least two different pathways, in order to stabilize the polymer. Unfortunately, this chemistry is applicable exclusively to poly(methyl methacrylate) and cannot be generalized.

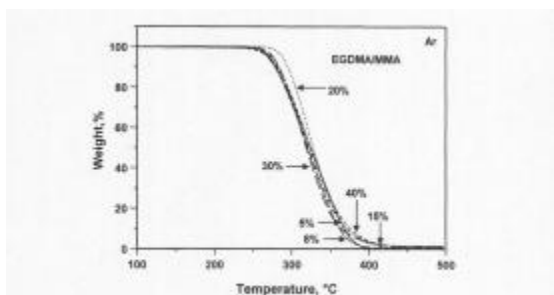


Fig. 7. TGA curves in inert atmosphere for copolymers of methyl methacrylate and ethylene glycol dimethacrylate. The numbers refer to the percentages of dimethacrylate in the feedstock.

Fig. 7. TGA curves in inert atmosphere for copolymers of methyl methacrylate and ethylene glycol dimethacrylate. The numbers refer to the percentages of dimethacrylate in the feedstock.

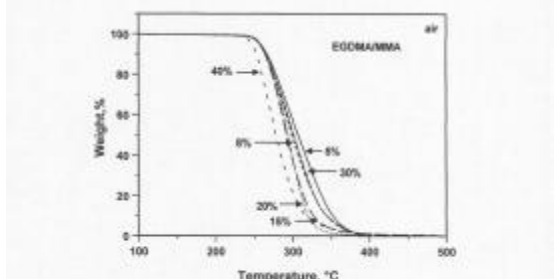


Fig. 8. TGA curves in air for copolymers of methyl methacrylate and ethylene glycol dimethacrylate. The numbers refer to the percentages of dimethacrylate in the feedstock.

Fig. 8. TGA curves in air for copolymers of methyl methacrylate and ethylene glycol dimethacrylate. The numbers refer to the percentages of dimethacrylate in the feedstock.

In the second section, graft copolymerization, a technique which may prove to be more generally applicable, is illustrated. If one can identify good char-- forming monomers, along with techniques to attach them to polymers, this could prove to be a very useful technique.

The strategy of using Friedel-Crafts chemistry to cross-link polystyrene has been shown to form char by both thermogravimetric analysis and radiative gasification, while cone calorimetry shows a greatly reduced rate of heat release.

Finally, the correlation between cross-linking and char formation seeks to provide information that will enable one to devise the most efficacious mode of cross-linking that can be used to enhance the thermal stability of a polymer. It has been shown that not all cross-linking leads to char formation, and information is beginning to emerge which can lead to useful chemical processes.

CONCLUDING COMMENTS

I have demonstrated some of the areas in which this research group has contributed to studies in fire retardancy. I wish to call to mind here that the focus of all of these investigations has been on developing basic knowledge on the mechanisms of condensed phase fire retardants. No effort has been made to approach the practical aspects of actually developing fire retardants: this task has been left for industry, It is hoped that the basic studies which we have performed will prove useful to the fire retardant industry and will lead to the development of more efficacious fire retardants.

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