

Interaction of Poly(Methyl Methacrylate) and Nafions

CHARLES A. WILKIE,*¹ JEFFRY R. THOMSEN,¹ and MARTIN L. MITTLEMAN²

¹Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233, and

²BP America Research, 4440 Warrensville Center Road, Cleveland, Ohio 44128

SYNOPSIS

The thermal degradation of Nafion-H, Nafion-K, and the mixture of each of these with poly(methyl methacrylate) (PMMA) has been studied. A mechanism is proposed for the thermal degradation of Nafion-H that involves an initial cleavage of the carbon-sulfur bond leading to SO₂, an OH radical and a carbon-based radical. This carbon-based radical then undergoes further degradation. The addition of PMMA to Nafion-H inhibits further degradation of the Nafion carbon-based radical and instead radical recombination reactions between PMMA fragments and this Nafion radical dominate the reaction scheme. The replacement of the hydrogen in Nafion-H with a potassium (i.e., Nafion-K) produces a much more robust material that does not degrade under conditions similar to those used for Nafion-H. Nafion-K has little effect on the degradation of PMMA.

INTRODUCTION

The thermal decomposition of PMMA has been studied by many workers.¹⁻⁹ The consensus is that it breaks down to give substantial amounts of monomer. PMMA prepared by a free-radical process has double bonds at the chain ends, and degradation is initiated at these sites at temperatures as low as 270°C. Polymer prepared anionically does not contain such double bonds, and degradation does not commence until 350°C. The identity of the pyrolysis products is believed to be little effected by an increase in temperature.^{10,11} The principal product of degradation is monomer produced by an unzipping reaction; most references cite PMMA as a polymer that produces exclusively monomer in its degradation.

In this laboratory, we have been concerned with developing an understanding of the thermal degradation of PMMA and in using that understanding to develop efficacious flame retardants for PMMA. We have investigated the reactions of several additives with the polymer and its models. Red phosphorus interacts with PMMA with the formation

of anhydride and methyl, methoxy phosphonium ions.^{12,13} The anhydride is formed only intramolecularly so the products are soluble. Since the red phosphorus investigation has established the carbonyl as the locus of reaction in the polymer, we next chose an additive that would be expected to interact effectively with this group. Wilkinson's salt, $\text{CIRh}(\text{PPh}_3)_3$, is well known to react with acyl halides, at room temperature, to form a rhodium carbonyl and an alkyl halide;¹⁴ thus it might be expected to react with an ester at elevated temperatures. Indeed, Wilkinson's salt does interact with PMMA by an oxidative addition process and leads to the formation of anhydrides.^{15,16} Of greatest interest is that these anhydrides are formed by an intermolecular process and thus are crosslinked. For reasons of toxicity, color, and expense Wilkinson's salt is not suitable as a flame retardant. Cobalt compounds were investigated in order to circumvent these problems. Two cobalt compounds that are known to function as hydrogenation catalysts, $\text{K}_4\text{Co}(\text{CN})_6$ and $\text{HCo}[\text{P}(\text{OPh})_3]_4$, have also been shown to effectively inhibit the degradation of the polymer.¹⁷

In this study we report on another route to crosslinked anhydride formation, reaction with strong acid. The strong acid that we have used is Nafion-H, a poly(tetrafluoroethylene) (PTFE) polymer containing pendant sulfonic acid groups. Nafion-H has a wide variety of commercial applications, these

* To whom correspondence should be addressed.

depend on the resistance of the material to chemical attack and to its selectivity, which allows cations, but not neutrals or anions, to migrate through a Nafion membrane.^{18,19} Catalytic reaction, such as alcohol dehydration and aromatic isomerizations, disproportionations, and alkylations are promoted by Nafion-H. The useful temperature range extends to about 190°C for short times.

RESULTS AND DISCUSSION

Degradation of PMMA

Previous work on the degradation of PMMA has suggested that only monomer is produced. When the degradation is carried out in a sealed tube at 375°C, we observe the formation of small amounts of CO, CO₂, CH₃OH, oligomers, a trace of anhydride, as well as monomer. A 1.0-g sample of polymer produces 56% monomer, 36% PMMA and nonvolatile oligomers, 6% CO₂, 1% CO and CH₄, 3% insolubles, and traces of methanol. A 2.0-g sample produces 44% monomer, 48% PMMA and nonvolatile oligomers, 5% CO₂, 1% CO and CH₄, and 2% insolubles. Infrared analysis of the PMMA fraction shows weak bands attributable to anhydride vibrations. Note that there is some difference in the product mix for a different charge to the vessel. A smaller sample leads to a greater yield of monomer and lower amounts of polymer. This is probably due to increased pressure forcing more reoligomerization.

The thermolysis of 1.0 g of monomer under identical conditions yields 64% monomer, 35% PMMA and nonvolatile oligomers, and 1% CO₂. Thus CO, methanol, anhydride, and most of the CO₂ must be produced by PMMA degradation, not from reactions of the monomer. Obviously, sealed tube reactions produce a different product mix than is obtained in open degradation. We conclude that in a sealed tube, PMMA degrades to monomer that may reoligomerize. The formation of CO and CO₂ must arise from decarbonylation and decarboxylation, presumably of the anhydride; methanol probably is a result of the loss of methoxy radical followed by hydrogen scavenging. It is worthwhile to note that photodegradation of PMMA produces similar products: CO, CO₂, CH₃OH, CH₄, and H₂. The formation of these products has been attributed to decomposition of the ester.²⁰ Presumably, ester degradation also occurs under thermal conditions in a sealed tube because the contact time is relatively long, while it does not occur under open conditions where the contact time is much shorter.

Degradation of Nafion-H

Little work has been reported on the degradation of Nafion-H. DuPont trade literature suggests that SO₂, CO₂, CO, HF, carbonyl fluorides, and fluorocarbons are produced. Some of these products must arise from degradation of the poly(tetrafluoroethylene) (PTFE) backbone. PTFE is one of the most thermally stable linear polymers. This thermal stability is attributed to the C-F bond strength and the shielding effect of the very electronegative fluorines. There is no significant degradation below 450°C, and even heating the polymer for 2 h at 500°C leads to only 30% weight loss. HF, SiF₄, CO, and CO₂ are produced at quite high temperatures. SiF₄ arises from the attack of HF upon glass. The proposed mechanism for thermal degradation of PTFE at modest temperatures proceeds by a random scission followed by formation of a difluorocarbene. This reactive carbene leads to the observed monomer and oligomeric products.²¹⁻²³

The study of Nafion-H degradation has been carried out both by sealed tube reactions and thermogravimetric analysis (TGA). Heating a 1.2-g sample of Nafion-H pellets to a temperature of 375°C for 2 h results in a 16% weight loss; the gases SO₂, CO₂, CO, and SiF₄ were detected. The beads are observed to fuse and significantly darken in these experiments; however, they remain hard.

Since the presence of sulfonic acids in Nafion-H produces its distinctive chemistry, attention must be paid to degradation of sulfonates. Ehlers et al.²⁴ subjected poly(arylene sulfonate) to thermal degradation in vacuum. They observe that SO₂ is evolved by cleavage of the C-S bond; the maximum evolution occurs between 250 and 350°C.

The TGA curve for Nafion-H is shown in Figure 1. There is little degradation until a temperature of about 380°C is reached. In these experiments the TGA was coupled to an FT-IR spectrometer, which permits the identification of the evolved gases.^{25,26} Between 35 and 280°C about 5% weight loss occurs, and the gases are identified as H₂O, SO₂, and CO₂. The water results from the fact that Nafion-H is quite hygroscopic; vacuum-dried films still retain 2.7% water. SO₂ results from cleavage of the C-S bond with the formation of a CF₂ radical and a SO₃H radical; this last radical may lose SO₂ and produce a hydroxyl radical. It is also possible that the OH radical is lost first. This is then followed by loss of SO₂ with the formation of the same CF₂ radical. A series of reactions (Scheme 1) has been suggested by a referee to account for the formation of CO₂. In this scheme an initial loss of water from the sulfonic

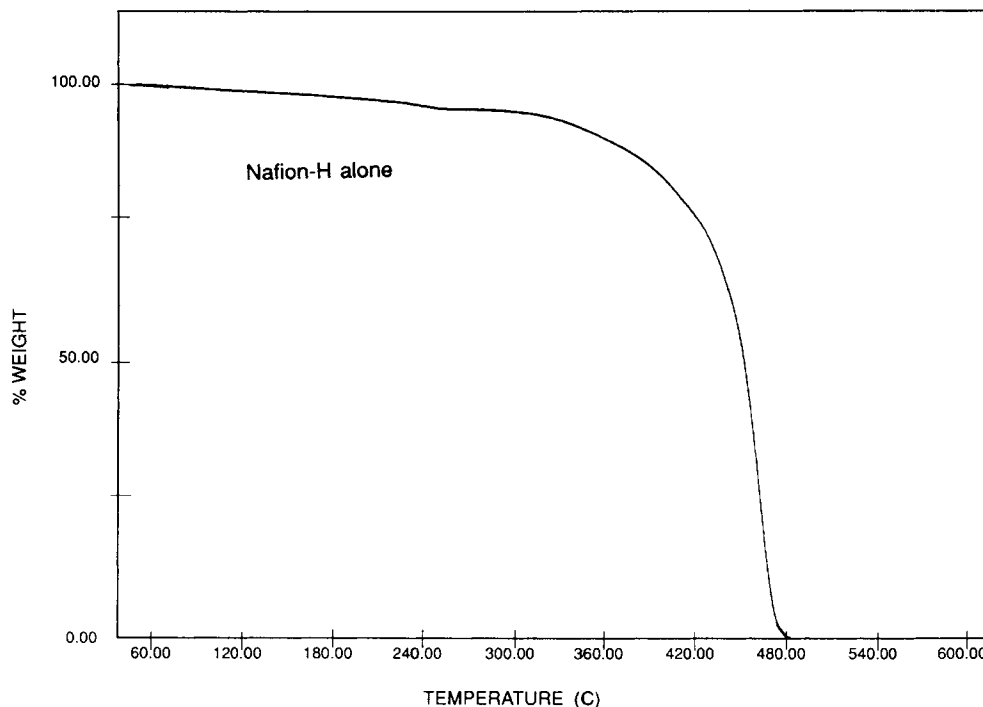
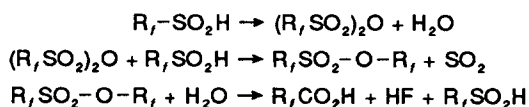


Figure 1 Thermogravimetric analysis curve for Nafion-H, run under inert atmosphere at a scan rate of 20°C/min.

acid produces anhydride, this anhydride may react with another sulfonic acid to produce a sulfonate ester.²⁷ Reaction of this ester with water will produce a carboxylic acid that can undergo decarboxylation to produce CO₂.

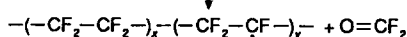
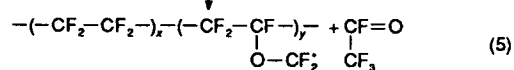
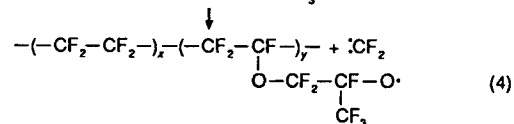
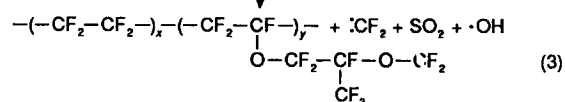
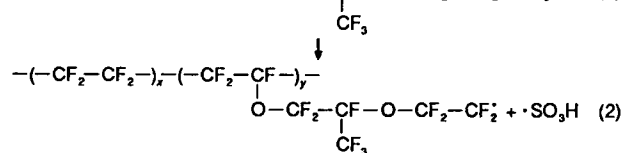
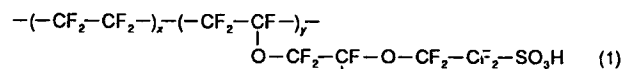
A weight loss of 7% is recorded between 280 and 355°C. The evolution of SO₂ and CO₂ increase throughout this region while that of water decreases. SiF₄ (1026 cm⁻¹), CO, HF, as well as substituted carbonyl fluorides (1957 and 1928 cm⁻¹) and absorbances in the C-F stretching region also appear in this region. At the highest temperatures, 355–560°C, 88% of the sample volatilizes. The amounts of SO₂ and CO decrease dramatically at 365°C and are no longer of consequence. The major absorbances in this temperature region are due to HF, SiF₄, carbonyl fluorides, and C-F stretching vibrations. A mechanism that accounts for these observations is presented in Scheme 2.

The bond that is initially broken is the C-S bond, giving a carbon-based radical and an SO₃H



Scheme 1

radical [Eq. (1), Scheme 2]. This last radical cleaves to produce SO₂, observed very early in the degradation, and a hydroxyl radical [Eq. (2)]. As previously noted, an alternate explanation is the initial cleavage of the S-O bond, forming an OH radical and a sulfur-based radical. This latter radical may



Scheme 2

then lose SO_2 giving the same CF_2 radical. The fluorocarbon radical [Eqs. (2) and (3)] loses two difluorocarbenes and produces an oxygen-based radical. This radical [Eq. (4)] may lose a substituted carbonyl fluoride and [Eq. (5)] carbonyl fluoride itself. The remaining polymer is now PTFE, which will degrade as noted earlier.

Interaction of Nafion-H and PMMA

There are some obvious differences between the thermolysis of the mixture compared to the sum of thermolysis of the individual components. The results from sealed tube reactions show that the amount of methyl methacrylate monomer is significantly decreased, more CO and CO_2 are obtained, and the amount of SO_2 may be reduced. An additional difference is that the infrared spectrum of the chloroform-soluble products of the reaction shows strong absorptions in the anhydride region (1805 , 1760 , 1020 cm^{-1}).

Thermolysis of a blend of 2.0 g PMMA and 1.2 g Nafion-H produces 4% CO and CH_4 , 19% CO_2 , 13% methyl methacrylate, 18% solubles, and 41% insolubles. Approximately the same amount of insolubles are recovered as the amount of Nafion charged to the system. Since it is known that SO_2 and C_2F_4 oligomers are lost, this suggests that the

mass that is added is roughly equivalent to that lost. To provide a comparison with PMMA alone, we shall indicate the fate of the polymer ignoring the amount of Nafion added. The 2.0 g of PMMA appear as 6% CO, 30% CO_2 (this fraction contains SO_2 also), 21% monomer, and 29% nonvolatile oligomers. This accounts for 86% of the PMMA charged to the vessel (actually less since some SO_2 is counted as CO_2) leaving at least 14% of the polymer incorporated with the Nafion. The pronounced decrease in monomer and oligomers must indicate that these materials are incorporated into the Nafion. Likewise the great increase in CO_2 leads to decarboxylated species, probably radicals, which may also combine with the Nafion. The reaction charge contains approximately 1 mmol of sulfonic acid groups and 0.1 mmol of polymer or 20 mmol of monomer units. Based upon these numbers, the maximum number of attachments is 1 Nafion to 20 monomer units or 10 Nafions per PMMA chain. This level of additive should lead to a retardation of monomer formation.

TGA/FT-IR studies of a blend prepared by casting a PMMA film onto a Nafion-H film also indicate a significant difference from that of the individual components. Both PMMA and Nafion-H have completely volatilized at 500°C ; the blend shows about 10% residue remaining at 600°C . The TGA of the blend is shown in Figure 2 and that of PMMA

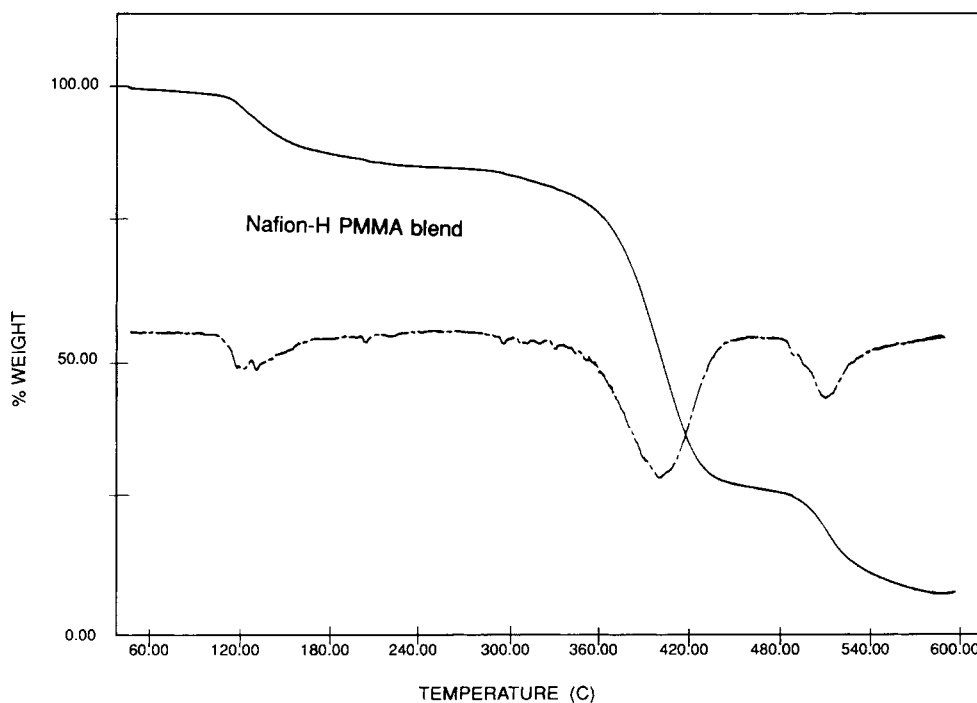


Figure 2 Thermogravimetric analysis curve for a blend of Nafion-H and PMMA, run under inert atmosphere at a scan rate of $20^\circ\text{C}/\text{min}$.

The presence of SO_2 suggests that the initial step is the cleavage of the C—S bond, generating a fluorocarbon radical and an SO_3H radical. The SO_3H radical yields SO_2 and a hydroxy radical. The absence of carbonyl fluorides indicates that propagation of radical sites along the Nafion chain is halted. The fluorocarbon radical may combine with a PMMA radical, as shown in Scheme 3. The decreased yield of fluorocarbon oligomers indicates that some of these CF_2 radicals do react in this way. An alternate reaction for the CF_2 radical is the loss of difluorocarbene, yielding PTFE oligomers and an oxygen-based radical. Radical propagation along the Nafion chain must cease at this point since carbonyl fluorides are absent. The cessation of radical propagation must arise by the stabilization of this oxygen-based radical, either by hydrogen abstraction from a PMMA methyl group or radical combination with a PMMA radical. Hydrogen abstraction from PMMA would yield a double bond that would be very susceptible to radical formation. This may lead to the possibility of Nafion attachment to both ends of a PMMA unit with a concomitant increase in stability. One must also note that the great amount of CO_2 that is produced indicates that some radical sites are produced on the polymer backbone by loss of carbomethoxy groups. These radicals would also be able to interact with the Nafion radical by radical

recombination. In any case one would expect that the PMMA fragments would be stabilized and less subject to depolymerization. The formation of anhydride must be attributed to the formation of the hydroxyl radical. This may interact with the ester functionality with the formation of methanol and lead to the production of anhydride.

Nafion-K Degradation

In order to verify these schemes Nafion-K was prepared and its interaction with PMMA examined. One may expect that the cleavage of the C—S bond will be more difficult for a potassium salt than for an acid, it has been shown that the thermal stability of amine arenesulfonates is greater than that of the corresponding sulfonic acids.²⁸ Sealed tube reactions show that no gases are lost from Nafion-K upon thermolysis, and the weight of material recovered is identical with that charged to the reaction vessel. Thus the C—S bond is much less susceptible to thermal cleavage.

Nafion-K is quite stable by TGA/FT-IR. The curve is shown in Figure 4. The onset of degradation is about 100°C higher than is observed for Nafion-H. A small amount of water is lost initially; there is no further weight loss until 390°C , and 88% of the material is volatilized between 390 and 535°C . The

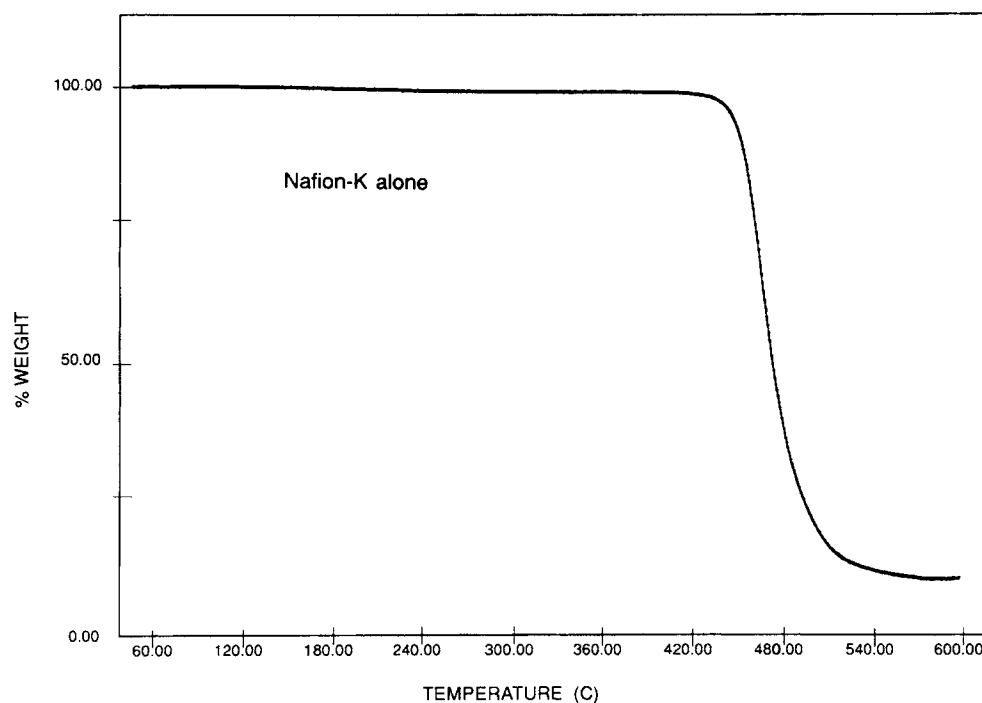


Figure 4 Thermogravimetric analysis curve for Nafion-K, run under inert atmosphere at a scan rate of $20^\circ\text{C}/\text{min}$.

only products that are observed are CO_2 , SiF_4 , and fluorinated hydrocarbons. No SO_2 is produced. The degradation of Nafion-K produces products more like those of PTFE than those of Nafion-H.

Interaction of Nafion-K and PMMA

The thermal degradation of blends of Nafion-K and PMMA were studied by sealed tube reactions and TGA/FT-IR. From sealed tube reactions, one may conclude that Nafion-K has no effect on the degradation of PMMA. Of the starting PMMA 42% is found as monomer and 49% as nonvolatile oligomers. No anhydride is found in these oligomers. These quantities are very similar to those produced from the thermolysis of PMMA alone.

For the TGA/FT-IR studies PMMA was cast onto Nafion-K films. An immediate difference is noted between Nafion-H and Nafion-K. One may quite easily cast an adherent coating of PMMA onto Nafion-H; however, acetone or chloroform solutions of PMMA do not wet the surface of the Nafion-K and one is left with a non-adherent coating. This suggests that the gross morphology of the potassium compound is quite different from that of the acid. Nafion-K is expected to behave as an ionomer with the potassium ions clustered at the center with a very hydrophobic surface of fluorocarbon. Nafion-

H, on the other hand, has a surface with both hydrophobic and hydrophilic groups, and the PMMA may interact with that surface. Casting of PMMA upon a Nafion-K surface could only be achieved by dipping the film into a solution and permitting the PMMA to completely encase the Nafion-K.

The TGA of the Nafion-K PMMA blend is shown in Figure 5. The amount of residue remaining at 600°C is the same as observed for Nafion-K alone. A small amount of degradation does occur at relatively low temperature; however, the curve is much more similar to that of Nafion-K than it is to PMMA. From ambient temperature up to 285°C , 4% of the sample volatilized. The material evolved consists of water, visible until about 280°C , and monomer, which begins to evolve at 235°C . Between 285 and 340°C the only material that is observed is monomer; 4% of the weight is lost in this region. In the third region, 340 – 410°C , 16% of the sample is lost. The gases consist only of monomer and CO_2 . Carbon dioxide appears at 350°C and steadily grows in intensity throughout this region. The bulk of the sample was lost in the highest temperature region, 66% volatilized between 410 and 550°C . The gases in this region were monomer, CO_2 , fluorocarbons, and SiF_4 . Monomer falls off rapidly at these temperatures and is replaced by fluorocarbons at 440°C . Carbon dioxide and fluorocarbons are observed until

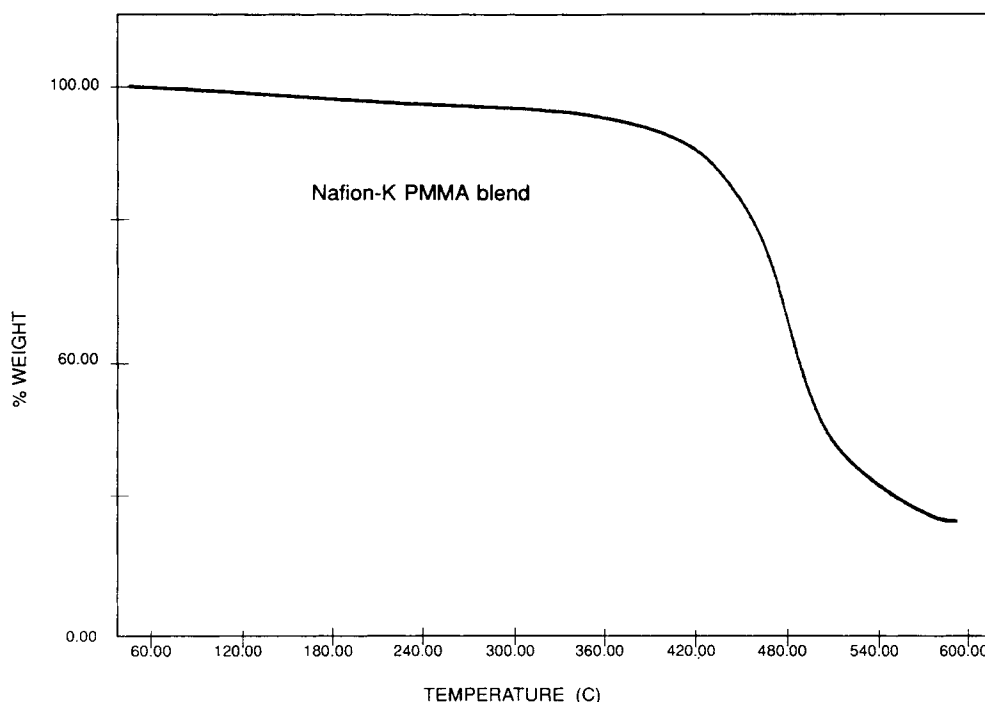


Figure 5 Thermogravimetric analysis curve for a blend of Nafion-K and PMMA, run under inert atmosphere at a scan rate of $20^\circ\text{C}/\text{min}$.

about 500°C. The only product that evolves above this temperature is SiF₄.

The sealed tube reactions indicate that there is essentially no effect by Nafion-K on PMMA degradation. The TGA studies do indicate some effect. The onset of degradation is at a higher temperature. Nonetheless degradation does still occur, and the products are identical with those observed in studies of the independent materials. This change is probably a result of physical, rather than chemical, effects since the quantity and identity of the products are unchanged at 375°C. Since the difference between Nafion-K and Nafion-H degradation is the absence of OH radical and SO₂ formation, and hence fluorocarbon radical formation, in Nafion-K, these species must be extremely important in PMMA stabilization by Nafion-H.

CONCLUSION

The degradation of Nafion-H proceeds by a radical pathway and initially produces a fluorocarbon radical, SO₂, and a hydroxyl radical. Both radicals effectively interact with PMMA and lead to stabilization. The fluorocarbon radical combines with PMMA radicals and produces a new, crosslinked, polymer. The hydroxyl radical interacts with the PMMA with the formation of anhydride units.

EXPERIMENTAL

Materials

Poly (methyl methacrylate) and Nafion-H were acquired from the Aldrich Chemical Company. Nafion-H beads and film were also kindly provided by E. I. DuPont Company. Solvents used were purchased from EM Scientific or Aldrich Chemical. TGA work was carried out using a Perkin-Elmer Model TGA-7 instrument. TGA/FT-IR work was performed on an Omnitherm horizontal balance TGA instrument interfaced to a Digilab FTS-60 FT-IR spectrometer with a heating rate of 10°C/min and a 50 cc/min flow of argon. Proton NMR spectra were obtained on a Varian EM360; ¹³C-NMR spectra were obtained on a JEOL FX60Q or a GE 300QE spectrometer. FT-IR spectra were obtained on a Analect FX 6200 spectrometer.

Thermolysis of PMMA

A 1.0-g sample of PMMA was placed in a standard vessel and thoroughly evacuated. After the vessel

was sealed off from the vacuum line, it was placed in an oven maintained at 375°C and heated for 2 h. After this time the vessel was removed from the oven and immediately cooled in liquid nitrogen. The vessel was then opened and the contents, 1.0 g, were removed. Some reactions were performed in break-seal equipped vessels. These were reattached to the vacuum line and opened, and the gases identified by infrared spectroscopy. *Caution: Vessels have been known to explode upon removal from the oven; care must be exercised.* A small amount of noncondensable gas was identified as CO and methane by IR. Condensable gases consisted of CO₂, monomeric methyl methacrylate, and traces of methanol. These were transferred to an open vessel and the CO₂ allowed to evaporate. The vessel was then removed from the vacuum line and treated with acetone or chloroform, yielding a soluble and an insoluble fraction. The soluble fraction showed a very weak anhydride absorption (1800, 1760, 1020 cm⁻¹). The 1.0-g sample of PMMA yielded 0.56 g monomer, 0.36 g PMMA and nonvolatile oligomers, 0.06 g CO₂, 0.36 mmol CO and CH₄, 0.03 g insolubles, and traces of methanol. Thermolysis of a 2.0-g sample gave 0.88 g monomer, 0.96 g PMMA and nonvolatile oligomers, 0.09 g CO₂, 0.52 mmol CO and CH₄, and 0.05 g insolubles.

Thermolysis of Nafion-H

A 1.2-g sample of Nafion-H pellets was placed in a standard break-seal vessel, thoroughly evacuated, and heated for 2 h at 375°C. The gases consisted of SO₂ (1325 cm⁻¹), CO₂ (2350 cm⁻¹), CO (2100 cm⁻¹), SiF₄ (1024 cm⁻¹), and fluorocarbons (1000–1400 cm⁻¹).

Preparation of Blends

For TGA and TGA/FT-IR work these blends were prepared by pouring a solution of PMMA in chloroform onto Nafion film and allowing the solvent to evaporate. For sealed tube reactions Nafion beads and PMMA powder were poured into a reaction vessel and mixed by shaking.

Thermolysis of a Blend of Nafion-H and PMMA

A 2.0-g sample of PMMA and 1.2 g of Nafion-H were combined in a standard break-seal vessel and treated as described earlier. The material contained 4.5 mmol CO and CH₄, 0.60 g CO₂, 0.42 g monomer, 0.57 g solubles, and 1.29 g insolubles. The soluble fraction shows strong anhydride vibrations in addition to the normal ester vibration. The infrared

spectrum of the insolubles shows both C—H and C—F stretching vibrations.

Preparation of Nafion-K

A sample of Nafion-H, either pellets or film, was stirred overnight with a 50% solution of aqueous KOH.

Thermolysis of Nafion-K

A 1.2-g sample of Nafion-K pellets was placed in a standard break-seal vessel and heated to 375°C for 2 h. No gases were detected upon reattachment to the vacuum line. After removal from the line 1.2 g of material was recovered.

Thermolysis of a Blend of Nafion-K and PMMA

A 2.0-g sample of PMMA and 1.2 g of Nafion-K were combined in a standard break-seal vessel and heated to 375°C for 2 h. The composition of the material in the vessel consisted of 0.84 g monomer, 0.97 g PMMA and oligomers, 1.2 g insolubles (Nafion-K), and traces of CO and CO₂.

REFERENCES

1. N. Grassie and H. W. Melville, *Disc. Far. Soc.*, **2**, 378 (1947).
2. N. Grassie and H. W. Melville, *Proc. Roy. Soc. Lond. A*, **199**, 14 (1949).
3. N. Grassie and H. W. Melville, *Proc. Roy. Soc. Lond. A*, **199**, 24 (1949).
4. H. H. G. Jellinek and M. D. Luh, *J. Phys. Chem.*, **70**, 3632 (1966).
5. I. C. McNeill, *Eur. Polym. J.*, **4**, 21 (1968).
6. G. Bagby, R. S. Lehrley, and J. C. Robb, *Polymer*, **10**, 83 (1969).
7. R. J. Gritter, M. Seeger, and D. E. Johnson, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 169 (1978).
8. F. Cullis and M. M. Hirschler, *The Combustion of Organic Polymers*, Clarendon Press, Oxford, 1981, pp. 139-141.
9. I. C. McNeill, in *Developments in Polymer Degradation*, N. Grassie, Ed., Applied Science, London, 1977, Vol. 1, p. 43.
10. S. L. Madorsky, *Thermal Degradation of Organic Polymers*, Wiley, New York, 1964.
11. J. R. MacCollum, *Makromol. Chem.*, **83**, 137 (1965).
12. C. A. Wilkie, J. W. Pettegrew, and C. E. Brown, *J. Polym. Sci., Polym. Lett. Ed.*, **19**, 409 (1981).
13. C. E. Brown, C. A. Wilkie, J. Smukalla, R. B. Cody, Jr., and J. A. Kinsinger, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 1297 (1986).
14. J. Tsuji, *Org. Syn. via Metal Carbonyls*, **2**, 595 (1977).
15. S. J. Sirdesai and C. A. Wilkie, *J. Appl. Polym. Sci.*, **37**, 863 (1989).
16. S. J. Sirdesai and C. A. Wilkie, *J. Appl. Polym. Sci.*, **37**, 1595 (1989).
17. C. A. Wilkie, S. J. Sirdesai, T. Suebsaeng, and P. Chang, *Fire Safety Journal*, **15**, 297 (1989).
18. S. J. Sondheimer, N. J. Bruce, and C. A. Fyfe, *Rev. Macromol. Chem. Phys.*, **C26**, 353 (1986).
19. F. J. Waller in *Polymeric Reagents and Catalysts*, W. T. Ford, Ed., American Chemical Symposium Series 308, Washington, D.C., 1986, p. 42.
20. N. Grassie and G. Scott, *Polymer Degradation and Stabilisation*, Cambridge University Press, Cambridge, 1985, pp. 72-77.
21. B. Wunderlich in *Thermal Characterization of Polymeric Materials*, E. A. Turi, Ed., Academic Press, New York, 1981, p. 221.
22. L. A. Errede, *J. Org. Chem.*, **27**, 3425 (1962).
23. M. Tutiya, *Japan J. Appl. Phys.*, **8**, 1356 (1969).
24. G. F. L. Ehlers, K. R. Fisch, and W. R. Powell, *J. Polym. Sci., Polym. Chem. Ed.*, **7**, 2969 (1969).
25. D. A. C. Compton, D. J. Johnson, and M. L. Mittleman, *Res. Dev.*, 142 (February 1989).
26. D. A. C. Compton, D. J. Johnson, and M. L. Mittleman, *Res. Dev.*, 68 (April 1989).
27. M. R. Tant, K. P. Darst, K. D. Lee, and W. C. Martin, "Multiphase Polymers: Blends and Ionomers, ACS Symposium Series 395," Chap. 15, 1989.
28. T. D. Kaczmarek, D. C. Phillips, and J. D. B. Smith, *Microchem. J.*, **22**, 15 (1977).

Received May 7, 1990

Accepted May 10, 1990