The Thermal Stability of Radiation-Grafted Poly(vinyl Chlorides)

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Synopsis

The thermal stability of radiation-grafted poly(vinyl chloride) (PVC) has been investigated by thermogravimetric analysis and compared with the thermal stability of the corresponding PVC polymer blends. Although both the grafting of methyl methacrylate and styrene and the blending of the corresponding homopolymers yield products of improved thermal stability as compared with unmodified PVC, the radiation grafting is somewhat more efficient for the stabilization of PVC than blending. Further, the rate of dehydrochlorination of PVC–g–styrene at relatively high temperatures exhibits a retardation, whereas that of unirradiated PVC show significant acceleration. A detailed study about a series of PVC–g–styrenes polymerized under various conditions shows that the retardation effect is more noticeable in the samples irradiated to 2.0–3.0 Mrad than in those irradiated to less than 1.0 Mrad. From the dose dependency, it has been suggested that the retardation effect is due to the interruption of the propagation of dehydrochlorination by branch sites produced by the radiation process. On the other hand, the graft copolymers of vinyl pyridines, PVC–poly(vinyl pyridine), and PVC irradiated in the presence of pyridine are much less stable than unmodified PVC. The instability is explained in terms of the substitution reaction with the bases and the base-catalyzed dehydrochlorination of PVC.

INTRODUCTION

Poly(vinyl chloride) (PVC) has become important as one of the less expensive flame-resistant plastic materials in the fields of wire insulations and cable jacketing[1–3] and in fiber and textile applications. Due to the effectiveness of the radiation process, radiation crosslinking[1,4] and radiation grafting[5–6] of PVC have been investigated extensively. The use of radiation, however, has some drawbacks. In particular, there is some question about thermal stability since radiation induces dehydrochlorination, which results in formation of additional initiation sites for thermal dehydrochlorination. It has been demonstrated recently that irradiation enhances thermal dehydrochlorination.[10,11] However, very few papers about the thermal stability of radiation-grafted copolymers of PVC have been published. In this work, we have attempted to learn more about the thermal stability of radiation-grafted copolymers of PVC.

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EXPERIMENTAL

An unplasticized commercial PVC (suspension polymerization, Sumilit SX-11, $\overline{\text{D.P.}}$ = 1100), supplied by Sumitomo Chemical Company, was precipitated from a tetrahydrofuran solution (2 g/100 ml) with methanol to remove any residual peroxide catalysts and suspension agents used in the polymerization process. After the precipitation, the PVC was washed repeatedly in methanol and dried in vacuo at room temperature. Tetrahydrofuran (Fisher certified) was distilled under nitrogen from potassium hydroxide in order to remove peroxides immediately before being used. A reagent-grade methanol (Fisher certified) was used as received. Methyl methacrylate, styrene, 2-vinylpyridine, 4-vinylpyridine, pyridine, and dimethylformamide was purified by distillation under nitrogen. These monomers and solvents were degassed and stored over calcium hydride in the absence of oxygen.

Radiation-grafted copolymers of PVC were prepared by mutual grafting in sealed glass ampoules. A weighed flake-like PVC was placed in the ampoule, degassed at room temperature for more than 24 hr, filled with the stored monomer by distillation on the vacuum line, and then sealed off under vacuum. Irradiation was carried out in a ^{60}Co source (U.S. Nuclear Corporation GR-9 irradiator). The dose rate was 0.55 Mrad/hr, and irradiation temperatures of 0°C and 25°C were used. After irradiation, the irradiated ampoules were opened, dissolved with tetrahydrofuran, precipitated with methanol, filtered through glass filters, and then washed with methanol.

In order to extract the homopolymers, graft copolymers of methyl methacrylate (PVC–g–methyl methacrylate) were washed with acetone, those of styrene (PVC–g–styrene) were washed with benzene, and those of 2-vinylpyridine and 4-vinylpyridine (PVC–g–2-vinylpyridine, PVC–g–4-vinylpyridine) were washed with methanol. After extraction of the homopolymers, the grafted samples were washed again with methanol and then dried at room temperature in vacuo for over one week.

Poly(2-vinylpyridine), poly(4-vinylpyridine), polystyrene, and poly(methyl methacrylate) were prepared by radiation bulk polymerization (25°C, 1.0–2.0 Mrad). The per cent grafting was taken to be the percentage increase in weight from the original weight.

The thermal stability of the PVC samples was determined by thermogravimetric analysis (TGA). TGA was carried out using a Perkin-Elmer TGS-1 thermobalance and in the form of a flake-like polymer precipitated from a tetrahydrofuran solution (2 g/100 ml) with methanol. A sample of 2–3 mg was placed in an aluminum pan, and the thermobalance chamber was flushed thoroughly with nitrogen before the start of each run. In the measurements of PVC polymer blends, a thin film was deposited on the aluminum pan by filling with mixed solutions of two polymers in tetrahydrofuran and by drying at 60°C for 24 hr after evaporating the solvent. During the run, nitrogen was passed through the chamber at a flow rate of 30 ml/min.

TGA was either isothermal (200°C, 240°C) or dynamic at a heating rate of 20°C/min. The temperature of the sample pan was calibrated with magnetic standards for both programmed temperature and isothermal studies by the method described by Salovey and Bair.[10]

RESULTS AND DISCUSSION

In order to obtain information about the thermal stability of radiation grafted PVC, three different types of vinyl monomers were investigated in this work: (1) methyl methacrylate, (2) styrene, and (3) vinylpyridine. Methyl methacrylate may be representative of the polyfunctional methacrylates which are well known as efficient crosslinking agents[1,4] for PVC. Since polystyrene is knonw to protect other polymers from radiation,[12] the styrene graft copolymers may receive the least radiation damage during the radiation grafting process. On the other hand, basic monomers such as vinylpyridine may catalyze radiation-induced and thermal dehydrochlorination of PVC, resulting in the low thermal stability of the graft copolymers. For example, pyridine and various amines are known to accelerate the dehydrochlorination process.[13,14]

Graft Copolymers of Methyl Methacrylate and Styrene

Figures 1 and 2 give dynamic TGA results for PVC–g–methyl methacrylate and PVC–g–styrene, compared with poly(methyl methacrylate),
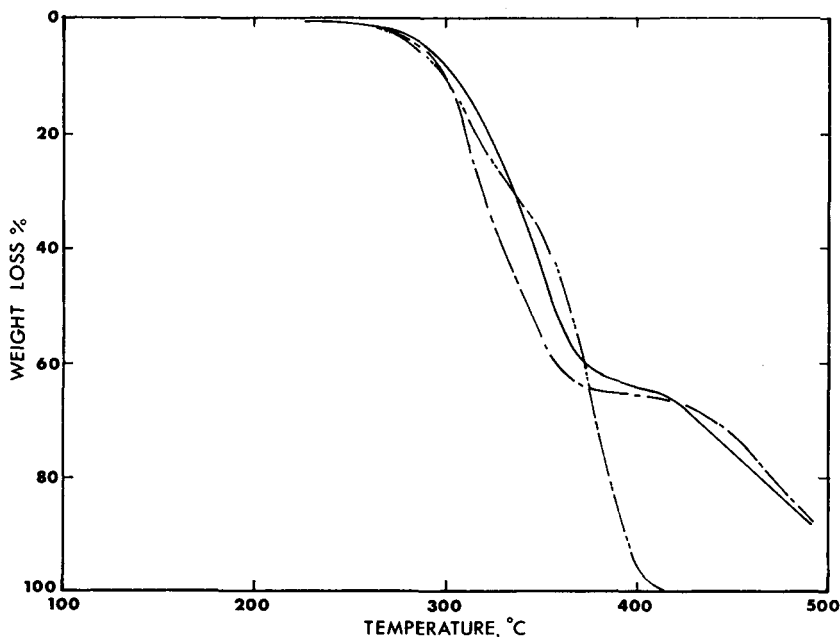

Fig. 1. Thermogravimetric analysis of PVC–g–methyl methacrylate at 20°C/min in nitrogen: (—·—) control PVC, irradiated at 25°C to 1.0 Mrad, and followed by the radical termination treatment; (—··—) poly(methyl methacrylate); (—) PVC–g–methyl methacrylate, irradiated at 25°C to 1.0 Mrad, grafting.
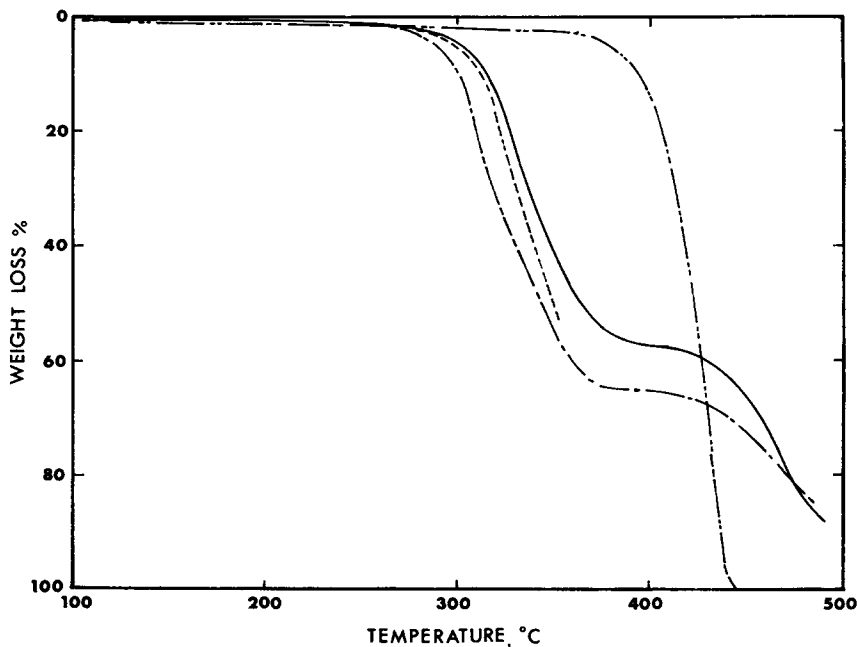
Fig. 2. Thermogravimetric analysis of PVC–g–styrene at 20°C/min in nitrogen: (—·—) control PVC, irradiated at 25°C to 1.0 Mrad, and followed by radical termination treatment; (—··—) polystyrene; (—) PVC–g–styrene, irradiated at 25°C to 1.0 Mrad, 25.8% grafting; dotted line refers to the PVC–g–styrene corrected for PVC component.

polystyrene, and an irradiated control PVC sample. The control PVC sample was irradiated in the absence of monomers to the same dose (1.0 Mrad) as the graft copolymers, dissolved with methyltetrahydrofuran in order to promote the termination of trapped free radicals before breaking the sealed ampoule. After being allowed to stand for several hours, the solution was precipitated with methanol and washed with methanol. The control PVC sample irradiated to 1.0 Mrad gave almost the same TGA curve as the unirradiated PVC, though similar samples irradiated to higher doses were less stable than the latter. From Figure 2 it is seen that polystyrene began to degrade at a much higher temperature (over 350°C) than the control PVC sample (250–260°C). In the thermal volatilization analysis accompanied by the differential condensation of styrene, for example, of a PVC–polystyrene polymer blend, it was observed that polystyrene breakdown occurs at higher temperature than PVC,[15] indicating that the degrading PVC does not initiate polystyrene breakdown at lower temperatures than normal. Consequently, the weight loss of PVC–g–styrene below 350°C may arise mainly from the dehydrochlorination of the PVC polymer chain. A dotted line in Figure 2 refers to the trace corrected for PVC component assuming that weight loss of polystyrene is absent below 350°C. As shown in Figure 2, PVC–g–styrene is apparently more stable than the control PVC. In Figure 1, the initial weight loss of the
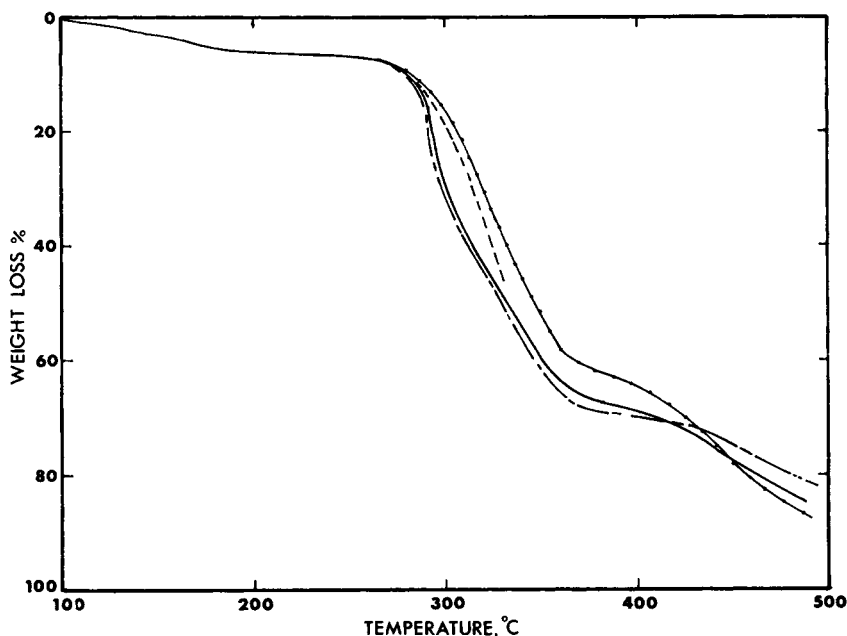
Fig. 3. Thermogravimetric analysis of the cast films (about 80 μ) of PVC polymer blends at 20°C/min in nitrogen: (— · —) unirradiated PVC; (—) PVC/poly(methyl methacrylate) = 80/20 polymer blend; (— · · —) PVC/polystyrene = 80/10 polymer blend; dotted line refers to the polymer blend corrected for PVC component.

poly(methyl methacrylate) is almost the same as the control PVC. The trace of PVC–g–methyl methacrylate is, nevertheless, at a slightly higher temperature in the initial stage (per cent weight loss of less than 30%) than both the control PVC and poly(methyl methacrylate). This indicates again that PVC–g–methyl methacrylate is slightly more stable than PVC.

There are three possible factors which affect the thermal stability of radiation-grafted copolymers of PVC: (1) interactions between PVC and the grafted second polymer component, (2) structural irregularities of the PVC polymer chain formed during the radiation process, and (3) branch sites produced by the grafting process. In order to obtain information about the first factor, the thermal stability of polymer blends corresponding to the graft copolymers was investigated. The dynamic TGA of the cast films of the polymer blends corresponding to the graft copolymers is shown in Figure 3. The thickness of the cast films was about 80 μ. A dotted line in Figure 3 means, again, the trace of the PVC–polystyrene polymer blend corrected for the PVC component assuming the weight loss of polystyrene is absent below 350°C. From Figure 3 it is seen that the mixing of polystyrene together with PVC retards the thermal dehydrochlorination of PVC. On the other hand, the mixing of poly(methyl methacrylate) gives a curve which is similar to that of the unirradiated PVC.

McNeill and Neil[15] investigated the thermal degradation of various polymer blends of PVC, using the thermal volatilization analysis with differential condensation, and found that the hydrogen chloride evolution is slightly retarded in all the blends involving PVC, indicating a slight stabilizing effect of the second polymer on the thermal dehydrochlorination. A more detailed study[15] of PVC–poly(methyl methacrylate) polymer blends showed that the hydrogen chloride evolution is appreciably delayed, even when small amounts of PMMA are present.

On the other hand, even small amounts of PVC initiate PMMA breakdown at lower temperatures than is normal. This interaction was explained in terms of attack on poly(methyl methacrylate) by chlorine atoms from the degrading PVC. In other words, a second polymer competes with PVC for chlorine atoms and acts as a chlorine atom scavenger. This explanation seems to be reasonable if a free-radical chain mechanism[4] involving chlorine atoms as a chain carrier is accepted.

Although the blending of polystyrene gives a product of improved thermal stability as well as the radiation grafting, it can be seen from Figures 1, 2, and 3 that the radiation grafting is somewhat more efficient than the blending of the corresponding homopolymer. This may be explained at least partly by an improved compatibility of the graft copolymers in terms of chlorine atoms scavenging by a second polymer.

The radiolysis of PVC and the subsequent dehydrochlorination produces allyl and polyenyl radicals[16,17] with thermally labile allylic chloride groups which remain even after the radical terminate. In the radiation grafting, since monomers act as a scavenger of the chlorine atom and PVC radicals, the scavenging reactions become competitive with the subsequent chain reaction of dehydrochlorination, which results in the decrease of allyl and polyenyl radicals with allylic chloride. The fact that the graft copolymers are more stable than the corresponding polymer blends indicates that the scavenging of chlorine atoms and PVC radicals by the monomers is very efficient and appreciable additional initiation sites such as allylic chlorides are not fomed if the radiation grafting process is limited to relatively low doses.

Effects of Polymerization Conditions

In a further study of the stabilizing effect of radiation grafting, a series of PVC–g–styrene prepared under various conditions was investigated by isothermal TGA. The isothermal TGA curves at 200°C and 240°C for a PVC–g–styrene (0°C, 3.0 Mrad, 46.5% grafting) are shown in Figures 4 and 5, compared with the corresponding control PVC (25°C, 3.0 Mrad) and the unirradiated PVC. In order to test the influence of trapped radicals and the resulting peroxides in irradiated PVC, one of the bulk irradiation samples was opened to air without any radical termination treatment and the isothermal TGA was measured in nitrogen after being exposed to air for several minutes. The isothermal TGA of another bulk irradiation sample was measured after carrying out the radical termination treatment with methyltetrahydrofuran described previously (control irradiated PVC
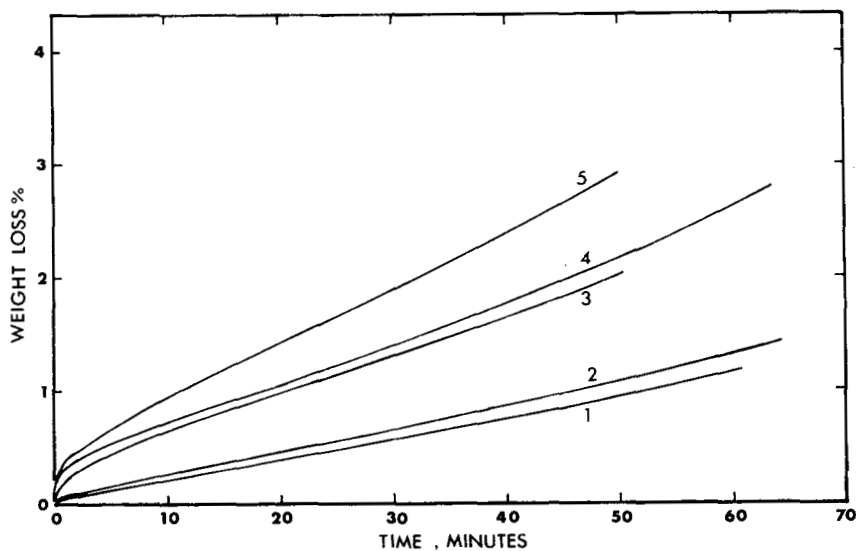
Fig. 4. Isothermal thermogravimetric analysis of PVC–g–styrene at 200°C in nitrogen: (1) PVC–g–styrene, irradiated at 0°C to 3.0 Mrad, 46.5% grafting; (2) unirradiated PVC; (3) control PVC, irradiated at 25°C to 3.0 Mrad, and followed by the radical termination treatment; (4) PVC irradiated at 25°C to 1.0 Mrad, without the radical termination treatment; (5) PVC irradiated at 25°C to 3.0 Mrad, without radical termination treatment.
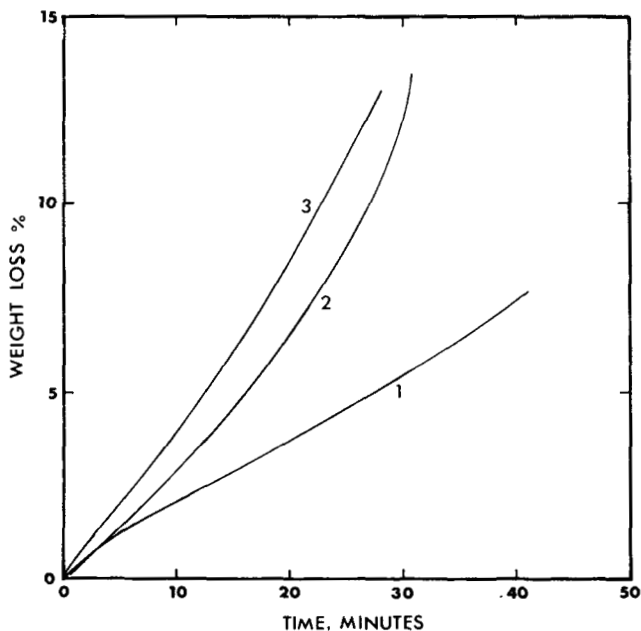

Fig. 5. Isothermal thermogravimetric analysis of PVC–g–styrene at 240°C in nitrogen: (1) PVC–g–styrene, irradiated at 0°C to 3.0 Mrad, 46.5% grafting; (2) unirradiated PVC; (3) control PVC, irradiated at 25°C to 3.0 Mrad, and followed by radical termination treatment.

TABLE I
Rates of Dehydrochlorination of PVC–g–Styrene[a]

	Irradiation temp., °C	Total dose, Mrad	Per cent grafting, %	Rate of dehydrochlorination $\times 10^6$/sec	
				200°C, 3 min	240°C, 15 min
Unirradiated PVC	—	—	—	4.8	71
PVC	25	1.0	—	5.9	74
PVC	25	3.1	—	10.5	90
PVC/styrene	25	0.3	10.8	3.6	49
PVC/styrene	25	1.0	25.8	2.5	26
PVC/styrene	25	2.2	59.6		58
PVC/styrene	25	3.0	88.4	5.5	51
PVC/styrene	0	2.2	29.0	4.7	33
PVC/styrene	0	3.0	46.5	4.1	32

[a] PVC was irradiated in pure styrene.

sample). As shown in Figure 4, the former is much less stable than the latter, indicating that trapped PVC radicals and the resulting peroxides in bulk irradiation PVC do initiate thermal dehydrochlorination. Following this result, only the sample in which the radicals had been terminated before breaking the sealed ampoule will hereinafter be discussed. In Figure 4, an initial weight loss in the former may be noted; this may be due to release of occluded hydrogen chloride since the other samples exhibit no initial weight loss. All the isothermal TGA data concerning PVC–g–styrene in this work were corrected for the PVC component, simply by subtracting the polystyrene component since there is no measurable weight loss of polystyrene at 200°C and 240°C. From Figure 5 it is seen that the rate of dehydrochlorination of the unirradiated PVC at 240°C exhibits a significant acceleration, whereas those of all the samples at 200°C are linear over a wide time range, as shown in Figure 4. On the other hand, the PVC–g–styrene gives a retardation in the initial stages rather than simply no acceleration. To evaluate this retardation effect, the rates of dehydrochlorination at 240°C, 15 min (at 8 mole-% of the total theoretical dehydrochlorination for the unirradiated PVC) were measured.

Table I gives the rates of dehydrochlorination at 200°C and 240°C for a series of PVC–g–styrene samples, in which PVC was irradiated in pure styrene to various doses. The rates of dehydrochlorination in Table I were calculated assuming that all the weight loss is due to the loss of hydrogen chloride, and they are expressed as the mole fraction of the total theoretical dehydrochlorination per second. As shown in Table I, all samples, except that irradiated to 3.0 Mrad at 25°C, are more stable than the unirradiated and the control PVC. With regard to the retardation effect observed at 240°C, it can be seen that the samples polymerized at 0°C exhibit a stronger retardation than samples polymerized at 25°C in spite of the much higher polystyrene concentration of the latter. These results indicate that the rates at 240°C depend not only on the polystyrene

TABLE II
Rates of Dehydrochlorination of PVC–g–styrene[a]

	Irradiation temp, °C	Total dose, Mrad	Per cent grafting, %	Rate of dehydro-chlorination, $\times 10^6$/sec	
				200°C, 3 min	250°C, 15 min
Unirradiated PVC	—	—	—	4.8	71
PVC/MTHF = 6/94	25	1.0	0	5.6	51
PVC/MTHF = 7/93	room temp.	2.0	0	9.8	103
PVC/MTHF = 7/93	15	3.0	0	24.6	
PVC/Styrene/MTHF = 6/34/60	25	0.30	7.2	4.0	36
PVC/Styrene/MTFH = 6/17/77	25	1.0	4.5	5.5	55
PVC/Styrene/MTHF = 6/8/86	25	2.0	3.7	7.2	32
PVC/Styrene/MTHF = 6/4/90	25	3.0	3.4	8.6	75
PVC/Styrene/MTHF = 6/17/77	0	3.0	4.8	6.9	33

[a] PVC was irradiated in methyltetrahydrofuran–styrene solutions.

concentration but also on another unknown factor. It is difficult to show this factor clearly in the samples irradiated in pure styrene since high dose samples contain high polystyrene concentrations.
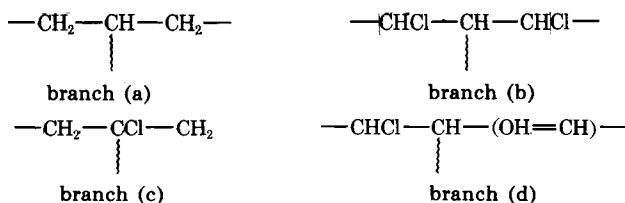
In order to demonstrate this factor more clearly, PVC was irradiated in methyltetrahydrofuran solutions containing various styrene concentrations. To prepare samples in which high dose samples contain low polystyrene concentration and vice versa, PVC–styrene–methyltetrahydrofuran solutions including low amount of styrene thus were irradiated to high doses and vice versa.

The results are summarized in Table II. It can be seen that polystyrene concentration decreases with increasing dose. The initiation sites of the thermal dehydrochlorination produced by irradiation increase with increasing dose. According to the radiation protection effect of aromatic compounds and the radical scavenging ability of monomers, high concentrations of styrene monomer in polymerization solution must give a lower number of the initiation sites. Samples with high polystyrene concentration should be more stable than samples with low polystyrene concentration according to the concept of chlorine atom scavenging by a second polymer during thermal degradation. Since the low-dose samples were irradiated in the polymerization solution of a high styrene concentration and contain a higher polystyrene concentration, it is expected that the low-dose samples would be more stable than high-dose samples. The results concerning the rates at 200°C in Table II are in accord with the discussion above since the rates increase with increasing dose and with decreasing styrene and polystyrene concentrations.

Surprisingly, the rates of dehydrochlorination at 240°C of samples irradiated to 2.0 Mrad are lower than the rates for the samples irradiated to 0.3 Mrad and 1.0 Mrad, despite the former containing lower polystyrene and styrene concentrations than the latter. Moreover, the sample irradiated to 3.0 Mrad at 0°C is much more stable than samples irradiated to 1.0 Mrad at 25°C in spite of the similarity of their polystyrene and styrene concentrations. From these results it is apparent that the retardation of the rates at 240°C increases with increasing dose. The structural changes in PVC polymer chain produced by radiation grafting may account for this dose dependence.

The radiolysis of PVC and the subsequent dehydrochlorination produce the following PVC radicals: (A) $—CH_2—\overset{\cdot}{C}H—CH_2—$, (B) $—CHCl—\overset{\cdot}{C}H—CHCl—$, (C) $—CH_2—\overset{\cdot}{C}Cl—CH_2—$, (D) $—CH=CH—\overset{\cdot}{C}H—CHCl$, (E) $—(CH=CH)_n—\overset{\cdot}{C}H—CHCl—$. The allyl and polyenyl radicals contain thermally labile allylic chlorine atoms, which initiate the thermal dehydrochlorination. The recombination of the polymer radicals (A), (B), (D), and (E) and reaction with monomer can lead to the formation of thermally stable branch sites with tertiary hydrogen atom. Radical (C), the only precursor of the thermally unstable branch site with tertiary chlorine atom, is a minor product in the radiolysis of PVC.[16]

The result in Table II which shows that the initial rates at 200°C increase with increasing dose indicates that the initiation sites such as allylic chloride increase with increasing dose. The fact that the rates at 240°C of high-dose samples exhibit retardation in spite of increasing initiation sites seems to indicate that the propagation of dehydrochlorination in the high-dose samples is lower than in the low-dose samples and the unirradiated sample. In other words, the retardation effect of the rates at relatively high temperature may be explained in terms of the interruption of the propagation of dehydrochlorination along the polymer chain by structural irregularities. As discussed above, other structural irregularities produced during radiation grafting are branch sites which result from crosslinking and grafting. According to the possible polymer radicals in irradiated PVC, there are four possible branches:

$$—CH_2—\underset{|}{CH}—CH_2— \qquad\qquad —CHCl—\underset{|}{CH}—CHCl—$$

branch (a)   branch (b)

$$—CH_2—\underset{|}{CCl}—CH_2 \qquad\qquad —CHCl—\underset{|}{CH}—(OH=CH)—$$

branch (c)   branch (d)

Branch (a) probably is the major product in the radiation grafting since radical (A), the precursor of branch (a), is the major radical in the radiolysis of PVC.

This viewpoint is supported by other findings. It has been observed, for example, that some radiation-polymerized PVC samples exhibit a lower rate of dehydrochlorination at relatively high temperatures than a com-

mercial PVC.[18] Further, it has been found that PVC irradiated in the presence of some additives exhibits a retardation effect similar to PVC–g–styrene.[19] These results also were explained[19,20] by assuming the interruption of the propagation of dehydrochlorination by additional branch sites produced during the radiation process.

Graft Copolymers of Vinylpyridines

Dynamic TGA curves for PVC–g–2-vinylpyridine and PVC–g–4-vinylpyridine are compared with the control PVC, poly(2-vinylpyridine), and poly(4-vinylpyridine) in Figures 6 and 7. From these figures it is seen that the major degradation of poly(2-vinylpyridine) and poly(4-vinylpyridine) occurs at much higher temperatures (over 350°C) than that of the control PVC. On the other hand, the initial weight loss of PVC–g–2-vinylpyridine and PVC–g–4-vinylpyridine takes place at much lower temperatures than that expected·in the absence of interaction between PVC and the graft component, and even that of the control PVC. Poly-(4-vinylpyridine) exhibits a slight weight loss between 100°C and 200°C, probably due to a small amount of residual monomer or solvent since a plateau is present between 220°C and 330°C. In an analogy with polystyrene, it is reasonable to assume that the early degradation of poly(vinyl-
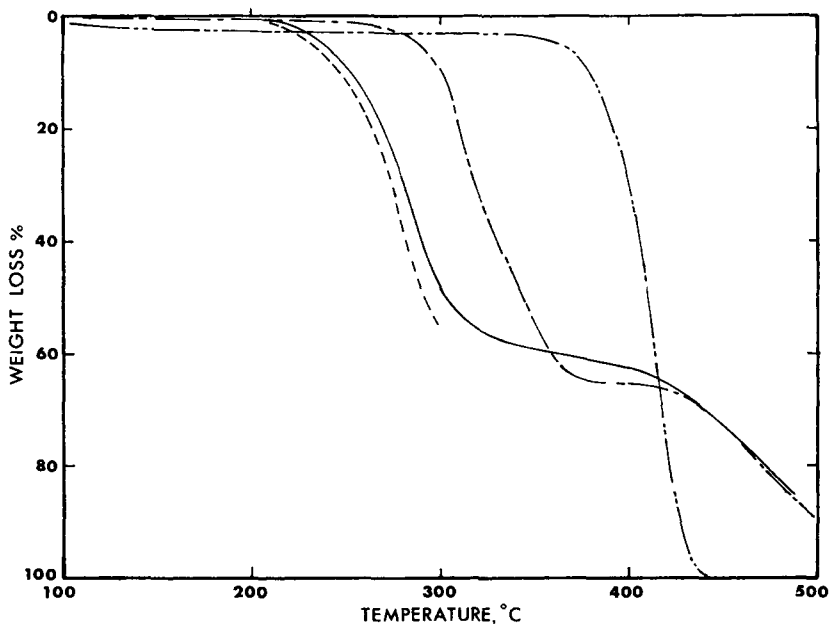

Fig. 6. Thermogravimetric analysis of PVC–g–2-vinylpyridine at 20°C/min in nitrogen: (———) control PVC, irradiated at 25°C to 1.0 Mrad, and followed by radical termination treatment; (—·—) poly(2-vinylpyridine); (——) PVC–g–2-vinylpyridine, irradiated at 25°C to 1.0 Mrad, 19% grafting; dotted line refers to the PVC–g–2-vinylpyridine corrected for PVC component.
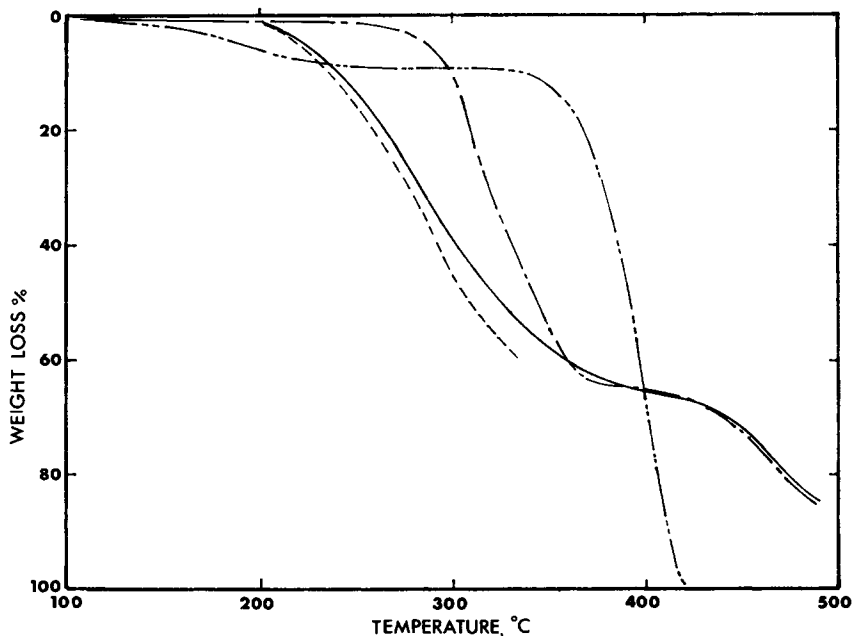
Fig. 7. Thermogravimetric analysis of PVC–g–4-vinylpyridine at 20°C/min in nitrogen: (—·—) control PVC, irradiated at 25°C to 1.0 Mrad, and followed by radical termination treatment; (—··—) poly(4-vinylpyridine); (—) PVC–g–4-vinylpyridine, irradiated at 25°C to 1.0 Mrad, 15% grafting; dotted line refers to the PVC–g–4-vinyl pyridine corrected for PVC component.

pyridine) is not influenced by the presence of the degraded PVC. A dotted line in Figures 6 and 7 again shows the data corrected for PVC component, provided the weight loss of the homopolymers is absent below 330°C. Thus, the weight loss of the graft copolymers at the low temperature may occur from dehydrochlorination of the PVC polymer chain.

Figure 8 shows the dynamic TGA of the cast films of a polymer blend [PVC/poly(2-vinylpyridine) = 80/20] corresponding to the graft copolymer, compared with the unirradiated PVC. From Figure 8 it is seen that the presence of poly(2-vinylpyridine) in PVC accelerates dehydrochlorination of PVC as well as the graft copolymer. However, the polymer blend begins to degrade at about 10°C higher temperature than the graft copolymer in Figure 6, though the cast film of unirradiated PVC in Figure 3 begins to degrade at about 10°C lower temperature than the flake-like PVC in Figure 6. It is apparent that the acceleration effect by poly(2-vinylpyridine) is somewhat less effective in the polymer blends than in the graft copolymers, which coincides with the results of methyl methacrylate and styrene. The difference may result from the radiation process.

In order to examine the effects of irradiation on the instability of PVC–g–vinylpyridine, the thermal stability of PVC irradiated in the presence
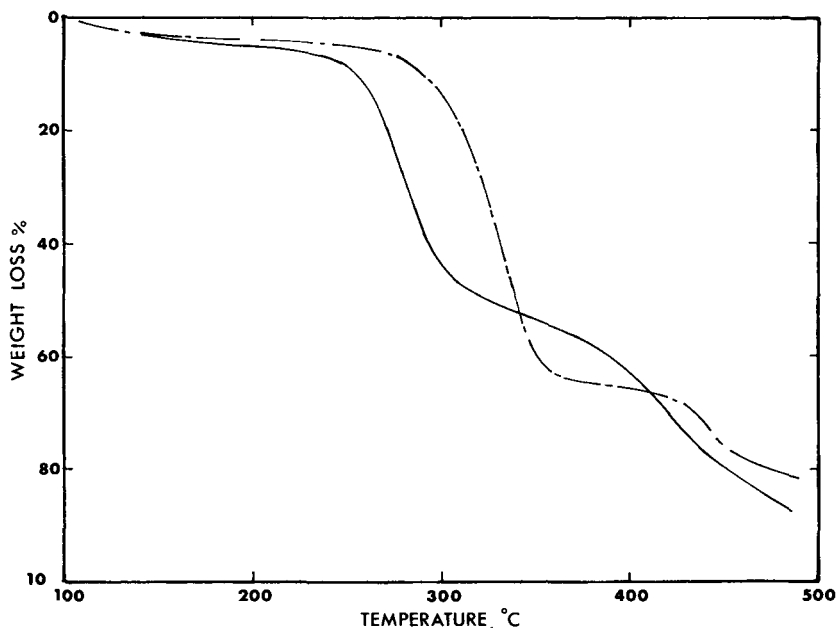
Fig. 8. Thermogravimetric analysis of cast films (about 30 μ) of PVC–poly(2-vinyl-pyridine) at 20°C/min in nitrogen: (—·—) unirradiated PVC; (—) PVC–poly(2-vinyl-pyridine) = 80/20 polymer blend.

of pyridine was investigated.   Figure 9 shows dynamic TGA results of PVC irradiated in a pyridine solution.   After irradiation, the irradiated polymer solution was dissolved with tetrahydrofuran, and precipitated and washed with methanol in a similar manner to the graft copolymers.   The weight change of PVC sample during the irradiation was less than 1%. Surprisingly, the sample irradiated in pyridine, nevertheless, gives a similar instability to the PVC–g–2-vinylpyridine (19% grafting).   In addition, PVC irradiated in benzene containing only 1% pyridine gave the same in-stability as the PVC irradiated in the pure pyridine solution.   In Figure 9, it is seen that an exhaustively purified and fractionated sample is still much more unstable than the control sample, though the treatment gives a little improvement in the thermal stability.   These results seem to indicate the presence of initiation sites for the thermal dehydrochlorination of the PVC chain which cannot be removed by purification.   The initiation sites may be N-vinylpyridinium chloride incorporated by the substitution reaction with pyridine or/and additional allylic chloride produced in larger amounts in the presence of pyridine.   However, it is uncertain whether the initiation sites are mainly formed by irradiation or not.

   Figure 10 shows isothermal TGA curves at 200°C for PVC precipitated similarly from a pyridine and a dimethylformamide solution without irra-diation, compared with those irradiated in pyridine and dimethylform-amide.   It is known that dimethylformamide accelerates[21] the thermal
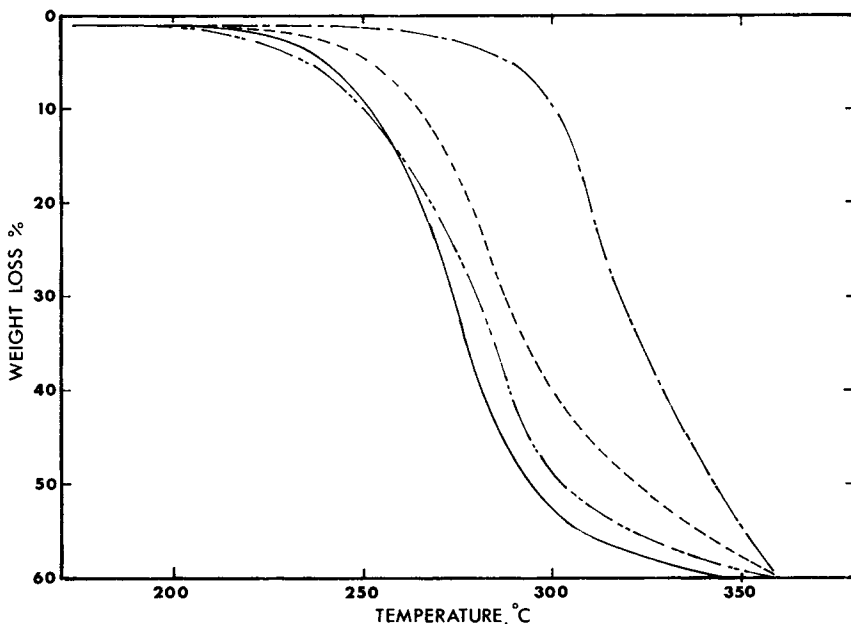
Fig. 9. Thermogravimetric analysis (20°C/min in nitrogen) of PVC irradiated in pyri-
dine: (—·—) control PVC, irradiated at 25°C to 1.0 Mrad, and followed by radical
termination treatment; (—··—) PVC–g–2-vinylpyridine, irradiated at 25°C to 1.0
Mrad, 19% grafting; (—) PVC irradiated in pyridine at 25°C to 1.0 Mrad; dotted line
refers to the irradiated PVC followed by a further fractionation with tetrahydrofuran
and methanol; only 4.4% of the original weight was recovered.

dehydrochlorination of PVC though it does not undergo a substitution
reaction such as that of PVC with weak bases.[13,14] From Figure 10 it is
seen that the rate of dehydrochlorination of the sample precipitated from
a pyridine solution without irradiation is much lower than that of the
sample with irradiation though the former is still more unstable than the
original PVC. On the other hand, the sample precipitated from a di-
methylformamide solution without irradiation exhibits almost the same
stability as the original PVC, whereas the sample with irradiation is much
less stable than the unirradiated PVC. Since the solubility of PVC is
similar for both and since dimethylformamide has a higher boiling point
than pyridine, it is unlikely that PVC precipitated from the pyridine solu-
tion contains more residue solvent than in the case of dimethylformamide.
Thus, these results indicate that the additional initiation sites are formed
to some degree in pyridine even without irradiation and at room tempera-
tures whereas DMF produce no additional initiation site without irradia-
tion. On the other hand, PVC irradiated in pyridine and dimethylform-
amide have a high concentration of initiation sites.

In the presence of a nucleophile or a base, alkyl halides undergo two
reactions, elimination (E2) or substitution (S_N2), and in most cases some
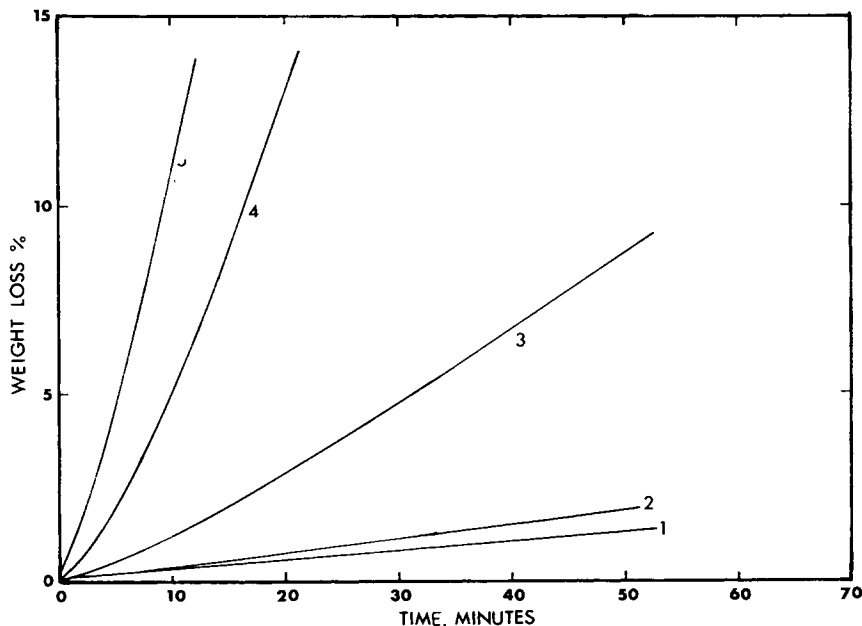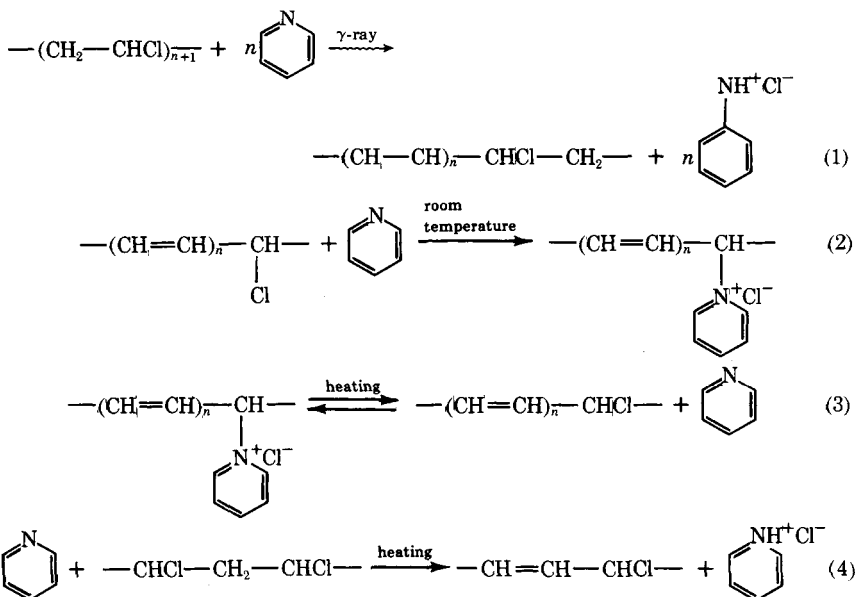
Fig. 10. Isothermal thermogravimetric analysis (at 200°C in nitrogen) of PVC irradiated in pyridine and dimethylformamide: (1) unirradiated PVC; (2) unirradiated PVC, precipitated from a dimethylformamide–tetrahydrofuran solution with methanol; (3) unirradiated PVC, precipitated from a pyridine–tetrahydrofuran solution with methanol; (4) PVC irradiated in dimethylformamide at 25°C to 1.0 Mrad; (5) PVC irradiated in pyridine at 25°C to 1.0 Mrad.

combination of the two processes occurs.[22,23] The same reactions occur in PVC. For instance, the dehydrochlorination (E2), which results in the formation of the conjugated polymers, occurs in PVC as treated with strong bases.[24,25,26] On the other hand, the treatments with weak bases, such as ethylenediamine–water at 100°C[13] and morpholine above 100°C,[14] mainly give substitution (S_N2). As to pyridine, when a pyridine solution of PVC is refluxed, substantial pyridine is not only incorporated into PVC but also the solution deepens in color, indicating the appearance of conjugated polymers.[27] Furthermore, it has been reported that in the mastication of PVC in the Brabender Plastograph, the presence of 2-vinylpyridine accelerated not only the dehydrochlorination during the mastication[28] but also the degradation of the resulting PVC after mastication.[29]

From the information cited above, it is evident that, in the presence of the pyridine group, PVC undergoes both the dehydrochlorination and the substitution reaction at relatively high temperatures. It has been reported[30] that γ-irradiation enhances the incorporation of morpholine into PVC, indicating the increase of the substitution reaction by irradiation. The enhancement by irradiation may indicate that the labile allylic chlorides, which are produced by radiation-induced dehydrochlorination, are

easily substituted by morpholine, though the author's explanation[30] is different from ours.

Agostini and Gatzke[26] reported that quaternary ammonium chloride $(C_2H_5)_4N^+Cl^-$ dissociates at 160°C and gives $(C_2H_5)_3N$ and C_2H_5Cl. According to this result, N-vinylpyridinium chloride formed by the substitution reaction may decompose and regenerate the pyridine groups over a certain temperature, which again catalyze the thermal dehydrochlorination. The allylic chlorides, which are produced by base-catalyzed dehydrochlorination, are thermally labile and can initiate the free-radical chain reaction of dehydrochlorination. A possible acceleration mechanism by pyridine groups is suggested as follows:

$$-(CH_2-CHCl)_{\overline{n+1}} + n\,\text{(pyridine)} \xrightarrow{\gamma\text{-ray}}$$

$$-(CH-CH)_n-CHCl-CH_2- + n\,\text{(aniline·NH}^+\text{Cl}^-) \quad (1)$$

$$-(CH=CH)_n-\underset{\overset{|}{Cl}}{CH}- + \text{(pyridine)} \xrightarrow[\text{temperature}]{\text{room}} -(CH=CH)_n-\underset{\overset{|}{N^+Cl^-}}{CH}- \quad (2)$$

$$-(CH=CH)_n-\underset{\overset{|}{N^+Cl^-}}{CH}- \underset{\text{heating}}{\overset{\text{heating}}{\rightleftharpoons}} -(CH=CH)_n-CHCl- + \text{(pyridine)} \quad (3)$$

$$\text{(pyridine)} + -CHCl-CH_2-CHCl- \xrightarrow{\text{heating}} -CH=CH-CHCl- + \text{(aniline·NH}^+\text{Cl}^-) \quad (4)$$

It is uncertain whether radiation-induced dehydrochlorination, reaction (1), is accelerated by pyridine. The graft copolymers of vinylpyridine include grafted poly(vinylpyridine) in addition to pyridine groups incorporated into PVC by the substitution. The grafted pyridine groups also accelerate the dehydrochlorination during the heating.

PVC irradiated at 25°C in dimethylformamide is much less stable than bulk-irradiated PVC. Since dimethylformamide does not undergo the substitution reaction, the acceleration of reaction (1) by dimethylformamide or incorporation of dimethylformamide or the fragments into PVC by radical reactions may be responsible for the thermal instability. Compounds with nitrile groups also accelerate the dehydrochlorination of PVC[29] and poly(vinylidene chloride).[31] In analogy with the instability of PVC irradiated in dimethylformamide, the thermal stability of graft copolymers of acrylamide, acrylonitrile, and the derivatives can also be expected to be unstable.

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