

Graft Copolymerization of Poly(vinyl Chloride) with Styrene. II. Thermal Behavior

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Synopsis

Thermal behavior of graft copolymers of polyvinyl chloride with polystyrene prepared by using a cationic initiator (AlCl_3) was evaluated by measurement of rates of dehydrochlorination in nitrogen atmosphere. With increase in the extent of grafting the rates were found to decrease. Dynamic thermogravimetric analysis revealed an overall improvement in thermal stability of copolymers. Development of polyene sequences in degraded polymer samples was evaluated by measurement of electronic absorption spectra. In comparison to PVC, graft copolymer samples had fewer conjugated double bonds.

INTRODUCTION

In recent years a number of papers have appeared regarding thermal behavior of graft copolymers of PVC with vinyl monomers. PVC-*g*-polybutadiene has been reported to be thermally superior to PVC.¹ Thame et al.^{2,3} have investigated thermal behavior of graft copolymers of PVC by using dynamic thermogravimetry and changes in electronic absorption spectra. They have explained the improvement in stability of PVC owing to the replacement of labile chlorine atoms by monomer units. Kennedy and Nakao⁴ have reported an improvement in stability of PVC-*g*-polystyrene in comparison to unmodified PVC. Synthesis of PVC-*g*-polystyrene has been reported in our earlier paper.⁵ In this work labile chlorine of PVC reacted preferentially with styrene monomer in the presence of AlCl_3 as an initiator. It will be of interest to study thermal behavior of these graft copolymers. Measurement of rate of dehydrochlorination can give information regarding thermal behavior of PVC. Thermogravimetric analysis (TGA), which gives information regarding the weight loss as a function of temperature, was also used to assess the thermal stability of graft copolymers. The structural changes taking place in the backbone (i.e., introduction of conjugated double bonds) were investigated by studies of electronic absorption spectra.

EXPERIMENTAL

PVC and PVC-*g*-polystyrene were the same as reported earlier.⁵

Rates of Dehydrochlorination Measurements. Known weights of polymer samples were dissolved in ethyl benzoate and then heated in nitrogen atmosphere at 200°C. The HCl evolved was estimated by titration against standard alkali.⁶

Thermogravimetric Analysis. A Stanton Redcroft TG-750 thermogravimetric analyzer was used; 5 ± 0.1 mg polymer sample was heated from room temperature to 700°C at a heating rate of 10°C/min.

TABLE I
Dependence of Rate of Dehydrochlorination on Concentration of PVC-*g*-Polystyrene in Ethyl Benzoate at 200°C in Nitrogen Atmosphere

Concentration of polymer, g/l.	$d\text{HCl}/dt$	
	(Mole acid evolved/ l. sec) $\times 10^6$	(Mole acid evolved/ g sec) $\times 10^7$
25	0.075	0.030
35	0.116	0.033
50	0.140	0.028
75	0.255	0.034

Differential Thermal Analysis. The DTA of the samples in nitrogen atmosphere was carried out using a Mettler 2000 instrument. In each experiment 7 ± 2 mg of the sample was heated from room temperature to 450°C at a heating rate of 10°C/min.

Electronic Absorption Spectra. A Unicam SP-700 spectrophotometer was used. Various polymer samples were degraded in ethyl benzoate (9 ± 1 g/l.) by heating at 200°C for 15, 30, 45, 60, 75, and 90 min before recording the spectra.

RESULTS AND DISCUSSION

Effect of Polymer Concentration on Rate of Dehydrochlorination

PVC-*g*-polystyrene sample having 34.5% graft-on was degraded in ethyl benzoate at 200°C. Four different polymer concentrations were used. The results are given in Table I. It is obvious from these results that amount of acid evolved per gram of polymer is almost constant.

Effect of % Graft-on on Rate of Dehydrochlorination

Polymer samples having 0.8, 8.0, 18.5, 27.5, and 34.5% graft-on were degraded at 200°C for 150 min. A polymer concentration of 50 g/l. was used. As the % graft-on increased, the rate of dehydrochlorination was found to decrease (Table

TABLE II
Dependence of Rate of Dehydrochlorination of PVC-*g*-Polystyrene on % Graft-on at 200°C in Ethyl Benzoate

Sample no.	% Graft-on	(Mole acid evolved/ l. sec) $\times 10^6$	(Mole acid evolved/ g sec) $\times 10^{7a}$
1	0	1.95	0.39
2	0.8	1.30	0.26
3	8.0	0.53	0.12
4	18.5	0.41	0.10
5	27.5	0.28	0.08
6	34.5	0.17	0.05

^a These values have been calculated on the basis of PVC in PVC-*g*-polystyrene.

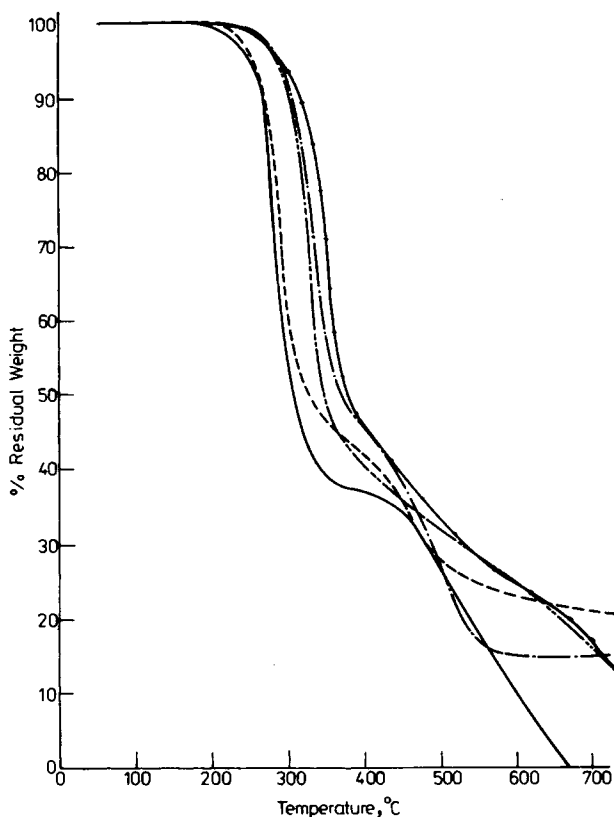


Fig. 1. Primary thermograms of PVC and PVC-*g*-polystyrene in nitrogen atmosphere: (—) % graft-on = 0, (---) % graft-on = 0.8; (- · -) % graft-on = 8.0; (- - -) % graft-on = 17.5; (—) % graft-on = 18.5.

II). Considerable reduction in dehydrochlorination rates was observed at even low % graft-on. Similar reductions in rates have been observed by Kennedy and Nakao at 165°C.⁴ However, these workers have reported an induction period prior to the acid evolution, and this induction period also increased with increase in % graft-on. Such an induction period was not observed at 200°C in the present work.

Thermogravimetric Analysis

Primary thermograms of various PVC and PVC-*g*-polystyrene samples are shown in Figures 1 and 2. A two-step decomposition was observed in PVC. Major volatilization started above 200°C. After a loss of nearly 60% of weight, the polymer attained a certain amount of stability above 350°C. A weight loss of 58.5% is expected on complete dehydrochlorination of PVC. Therefore, it may be concluded that in this temperature range, HCl is the predominant product of degradation. Further degradation of PVC begins above 450°C and almost all the sample is lost around 660°C. This distinct two-step behavior of PVC degradation is gradually lost as the % graft-on is increased in the graft copolymers.

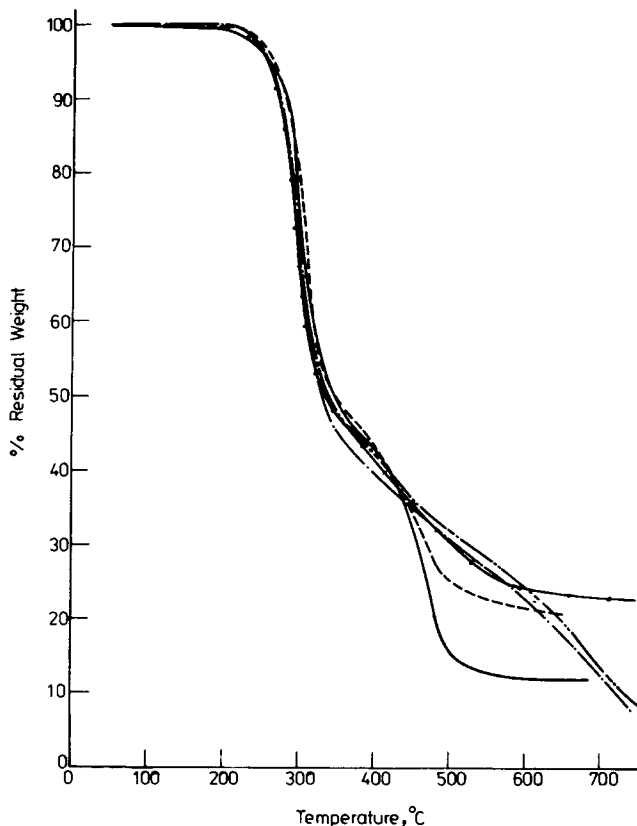


Fig. 2. Primary thermograms of PVC-g-polystyrene in nitrogen atmosphere: (—) % graft-on = 22.0; (---) % graft-on = 25.0; (- · -) % graft-on = 25.6; (- - -) % graft-on = 31.0; (— · —) % graft-on = 34.0.

The temperatures corresponding to initial decomposition (IDT), 50% decomposition (T_{50}), and integral procedural decomposition temperature (IPDT)⁷ were calculated from the primary thermograms and are given in Table III. IDT values of grafted copolymers were $\approx 30^\circ\text{C}$ higher than those of the unmodified PVC. However, an increase in % graft-on did not affect the IDT. Similarly, T_{50} also increased to $325\text{--}365^\circ\text{C}$ from 310°C on graft copolymerization of PVC. A significant increase in IPDT was observed in graft copolymers. The IPDT values increased with increase in % graft-on up to 17.5%; a further increase in % graft-on did not affect IPDT in a systematic manner.

Differential Thermal Analysis

DTA thermograms were recorded up to a temperature of 450°C . A shift in baseline indicative of T_g is not very well resolved (Fig. 3). Kennedy and Nakao⁴ have reported a T_g of $91\text{--}99^\circ\text{C}$ for polystyrene and of 73°C for PVC. With a physical blend of PVC and polystyrene two separate transitions were observed at 73 and 93°C , and a graft copolymer sample exhibited only one transition. In the present work, only a broad shift was observed in the temperature range of $60\text{--}100^\circ\text{C}$. It is, however, difficult to assign a T_g value on the basis of these thermograms.

TABLE III
Results of Thermogravimetric Analysis of PVC and PVC-*g*-Polystyrene in Nitrogen Atmosphere

Sample no.	% Graft-on	IDT, ^a °C	T ₅₀ , ^b °C	IPDT, ^c °C
1	0	200	310	335
2	0.8	230	325	409
3	8.0	230	365	425
4	17.5	225	347	432
5	18.5	230	330	409
6	22.0	225	350	397
7	25.0	230	345	415
8	25.6	230	330	389
9	31.0	230	340	423
10	34.0	230	335	417

^a IDT = initial decomposition temperature.

^b T₅₀ = Temperature of 50% loss in weight.

^c IPDT = Integral procedural decomposition temperature.

A broad endothermic shift was observed in the temperature range of 100–250°C. This may be due to an increase in the mobility of polymer chains above T_g . A sharp endothermic maximum was observed at 310°C, which also corresponds to the temperature of maximum weight loss in TGA. This endothermic peak may therefore be due to the dehydrochlorination of PVC. An exotherm was observed at about 390–410°C and may be due to the cyclization and chain scission of conjugated polyene chains.⁸ The temperatures of various exothermic and endothermic transitions are given in Table IV.

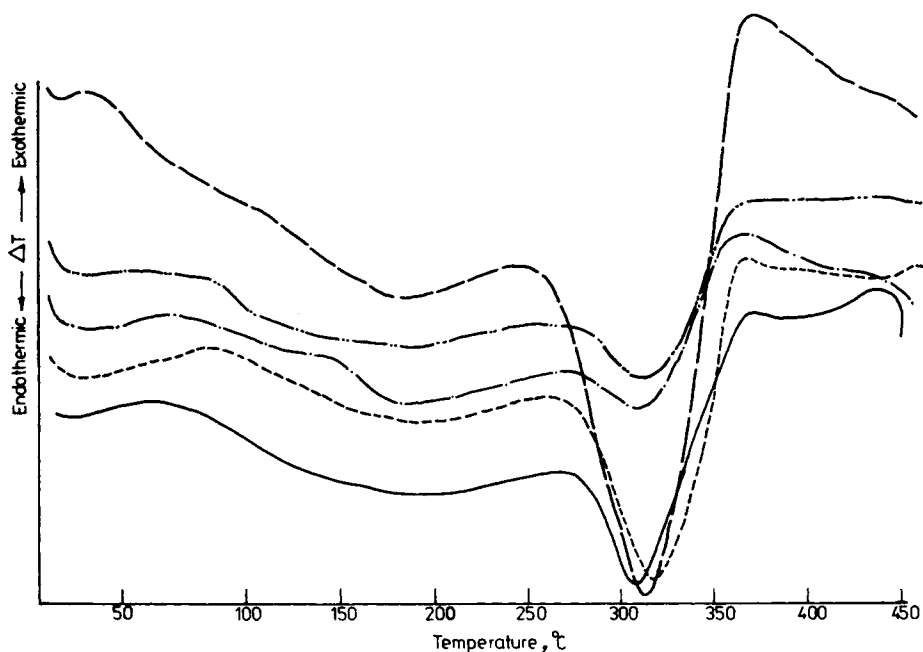


Fig. 3. DTA thermograms of PVC-*g*-polystyrene and PVC: (—) % graft-on = 0; (---) % graft-on = 0.8; (- · -) % graft-on = 8.0; (- - -) % graft-on = 25.6; (- - -) % graft-on = 31.0.

TABLE IV
Results of Differential Thermal Analysis of PVC-*g*-Polystyrene Samples

% Graft-on	Temperatures of endothermic (-) and exothermic (+) transitions, °C
0	(-) 310, (+) 370
0.8	(-) 305, (+) 360
8.0	(-) 310, (+) 360
17.5	(-) 310, (+) 360
18.5	(-) 310, (+) 350
22.0	(-) 320, (+) 350
25.0	(-) 310, (+) 360
25.6	(-) 310, (+) 360
31.0	(-) 305, (+) 360
34.0	(-) 310, (+) 360

Electronic Absorption Spectra

Samples having 18.5 and 31.0% graft-on were heated in ethyl benzoate for definite intervals of time and their spectra were then recorded at room temperature (Figs. 4 and 5). E' in these plots is obtained by dividing the observed optical density by the cell concentration (in g/dl). This was done to take into consideration slight variations in the concentration of samples. It is obvious that E' increased as the time of heating was increased from 15 to 75 min. Total number of polyenes (T_n), total number of double bonds (D_n), and % of double bonds (P_n) present in the degraded samples were calculated by the procedure described earlier.⁹ These values for various samples are given in Table V. In comparison to PVC, grafted samples had fewer conjugated double bonds.

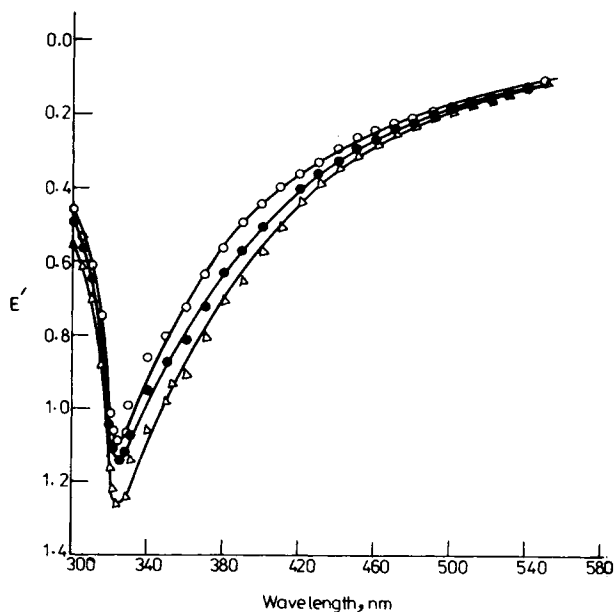


Fig. 4. Absorption spectra of PVC-*g*-polystyrene (18.5% graft-on) degraded in ethyl benzoate at 200°C: (O) 15 min; (●) 45 min; (▲) 75 min.

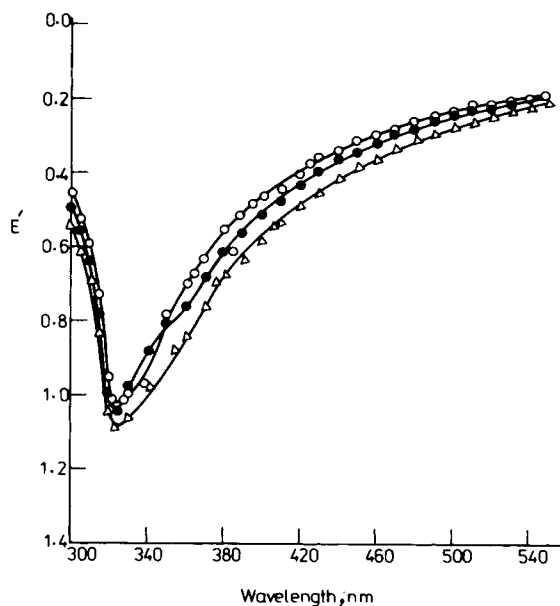


Fig. 5. Absorption spectra of PVC-*g*-polystyrene (31.0% graft-on) degraded in ethyl benzoate at 200°C: (○) 15 min; (●) 45 min; (▲) 75 min.

On the basis of these results it can be concluded that PVC grafted with polystyrene in the presence of AlCl_3 is thermally superior to the unmodified polymer. The effect of the increase in the extent of grafting on thermal stability is not very significant, and a sample with 18% graft-on attains an optimum stability.

TABLE V
Effect of Heating Time on Total Number of Conjugated Polyene Sequences (T_n), Total Number of Double Bonds (D_n), and Percentage of Double Bonds (P_n) in PVC and PVC-*g*-Polystyrene Samples Degraded in Ethyl Benzoate at 200°C in Nitrogen Atmosphere

% Graft-on	Time of heating, min	T_n	D_n	P_n
0	30	0.2956	2.1846	0.1409
	60	0.3765	2.6969	0.1739
	90	0.4331	3.0961	0.1997
	120	0.4077	2.9078	0.1876
18.5	15	0.1319	0.9475	0.0610
	30	0.1393	1.0075	0.0650
	45	0.1420	1.0185	0.0660
	60	0.1440	1.0349	0.0670
	75	0.1537	1.0940	0.0710
31.0	90	0.1623	1.1696	0.0750
	15	0.1313	0.9520	0.0610
	30	0.1323	0.9615	0.0620
	45	0.1430	1.0409	0.0670
	60	0.1453	1.0587	0.0680
	75	0.1574	1.1499	0.0740
	90	0.1585	1.1585	0.0750

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