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## Polyvinyl Chloride-g-Styrene): Synthesis, Characterization, and Physical Properties

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## **Poly(vinyl Chloride-g-Styrene): Synthesis, Characterization, and Physical Properties**

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### ABSTRACT

The synthesis, characterization and some physical properties of poly(vinyl chloride-g-styrene) are described. The graft copolymer was prepared by initiating the polymerization of styrene with poly(vinyl chloride) in conjunction with  $\text{Et}_2\text{AlCl}$ . Graft copolymer characterization involved GPC,  $T_g$ , heat stability, and intrinsic viscosity studies. Among the physical properties stress-strain and impact strength measurements have been carried out.

### INTRODUCTION

In the course of our fundamental studies on sequential copolymers produced by cationic techniques [1] we became interested in the synthesis of poly(vinyl chloride-g-styrene), PVC-g-PSt, and in the exploration of some physical-mechanical properties of this material. While PVC-g-PSt has previously been prepared by anionic polymerization methods [2-4], the properties of the graft have not been described. Attempts to produce this graft copolymer have also been

made by Plesch [5, 6] who used  $\text{AlCl}_3$  and  $\text{TiCl}_4$  to cointiate the polymerization of styrene from PVC backbone, however, the products were ill defined mixtures, and little characterization work was reported. The discovery of Kennedy and Baldwin [7] pointed the way toward a better synthesis route, namely the cointiation of styrene polymerization by alkylaluminum compounds and PVC.

## EXPERIMENTAL

### Materials

PVC (Geon 103-EP, B. F. Goodrich Co.) was reprecipitated three times with using THF and methanol. Styrene (Eastman Kodak Co.) and  $\text{Et}_2\text{AlCl}$  (Ethyl Corp.) were freshly distilled under reduced pressure.

### Graft Copolymerization

Polymerization and material transfers were carried out in a dry box under a nitrogen atmosphere (moisture level  $10^{1-30}$  ppm). Purified PVC was dissolved in 1,2-dichloroethane (1,2-DCE) and cooled, and prechilled monomer was added to the stirred solution. All experiments were carried out in homogeneous solutions. Polymerization was terminated by the addition of methanol, the crude product precipitated into excess methanol, filtered, dried, and fractionated.

### Fractional Precipitation

A solution of 15 g crude product was dissolved in 1500 ml THF, and petroleum ether (boiling range  $39-50^\circ\text{C}$ ) was added dropwise. Rapid stirring and slow precipitant addition prevented local precipitation. At the onset of precipitation, after a slight permanent haziness developed, stirring was discontinued and the system stored for 24 hr. The precipitated material was collected by centrifugation and further purified by reprecipitation and drying in vacuo at room temperature. The above operation was continued until all dissolved polymer was recovered. The composition of each fraction was determined by ir analysis.

### Infrared Analysis

The PST content of the fractions was determined by IR spectroscopy by using a Perkin-Elmer 521 grating infrared spectrophotometer and

compression-molded transparent films of 100-130  $\mu\text{m}$  thickness. A calibration plot was constructed and the absorptivity  $a$  of PVC/PSt blends of known composition was determined. The homogeneous, finely powdered blends were dissolved in THF, coprecipitated into methanol, and dried. The absorptivity was measured by noting the absorbance of PSt at  $1940\text{ cm}^{-1}$ .

### Gel Permeation Chromatography

GPC analysis was carried out by using a Waters Association GPC Instrument 200 with four columns of various pore sizes:  $7 \times 10^5 - 5 \times 10^6 \text{ \AA}$ ,  $5 \times 10^4 - 1.5 \times 10^5 \text{ \AA}$ ,  $5 \times 10^3 - 1.5 \times 10^4 \text{ \AA}$ ,  $700 - 2000 \text{ \AA}$  equipped with differential refractometer and UV spectrophotometer (at  $254\text{ nm}$ ). The solvent was THF, and 0.63% solutions were used at  $25^\circ\text{C}$ . In some cases, we also used at  $30^\circ\text{C}$  a high resolution GPC instrument (Waters Ana-Prep Instrument) equipped with seven columns (pore sizes):  $7 \times 10^5 - 5 \times 10^6 \text{ \AA}$ ,  $1.5 \times 10^5 - 7 \times 10^5 \text{ \AA}$ ,  $5 \times 10^4 - 1.5 \times 10^5 \text{ \AA}$ ,  $1.5 \times 10^4 - 5 \times 10^4 \text{ \AA}$ ,  $5 \times 10^3 - 1.5 \times 10^4 \text{ \AA}$ ,  $5 \times 10^3 - 1.5 \times 10^4 \text{ \AA}$ ,  $2000 - 5000 \text{ \AA}$ ) and a differential refractometer.

### Thermal Stability Studies

The rate of HCl evolution was determined by alkalimetric titration by using a slightly modified ASTM method D-793-49 [8].

### Intrinsic Viscosity

An Ubbelohde viscometer and THF solvent were used at various temperatures.

### Mechanical Properties

Stress-strain response was determined by an Instron Tester and microdumbbells die-cut from films cast from 3% solutions in THF. The strain rate was  $1\text{ cm/min}$  at  $25^\circ\text{C}$ . Dynamic properties were determined with a Rheovibron (Toyo Measuring Instruments, Ltd.) instrument by use of a heating rate of  $3^\circ\text{C/min}$  and  $110\text{ cycles/min}$ . Impact strength was determined by ASTM D-256-56.

## RESULTS AND DISCUSSION

Synthesis and Fractionation

PVC-g-PSt graft polymers of various compositions were prepared by dissolving PVC in 1,2-DCE, adding styrene to the cooled solution and coinitiating the grafting by  $\text{Et}_2\text{AlCl}$ . Grafting ensued rapidly and the reaction was terminated by the addition of methanol. The crude product was washed with methanol, filtered, dried and weighed to determine overall conversion, and subsequently fractionated to remove homopolymer(s). Table 1 is a summary of synthesis conditions and results. Rate of grafting increased with the concentration of  $\text{Et}_2\text{AlCl}$ , styrene, and PVC and with temperature.

Subsequent to small-scale orienting runs, larger amounts of graft copolymers were prepared for characterization and physical property studies. Fractional precipitation from THF solution with petroleum ether precipitant was used to purify the grafts and to determine grafting efficiencies (GE). This solvent/precipitant system was chosen such that ungrafted PVC should precipitate first, followed by PVC-g-PSt, and finally by PSt.

Prior to graft fractionation, we determined the effect of PVC and PSt concentration and that of PSt molecular weight on the precipitation point  $\gamma$  (the volume ratio of precipitant and solvent at the onset of the first noticeable precipitation). The precipitation points of PVC and PSt were  $\sim 1.0$  and  $\sim 2.0$ , respectively (below  $\sim 2\%$  PVC or PSt, and below  $\sim 15,200$  number-average molecular weight of PSt, the precipitation points increased).

None of the fractionations yielded solid precipitate at  $\gamma = 1.0 \pm 0.30$ , indicating the essential absence of ungrafted PVC. Fractions which precipitated between  $\gamma = 1.3$  and  $1.5$  were combined and used in characterization studies. GPC indicated uniform PSt distribution over the fractions. Fractionation indicated the presence of large amounts of PSt (20-70%) in the system which may be due to protic impurities and/or chain transfer to monomer during grafting.

Thermal Stability

PVC is quite heat-sensitive, and a large amount of work has been directed to understand the reason(s) of PVC heat sensitivity and to find ways to improve this deficiency. Previous work [9-14] has shown that cationic grafting greatly improves thermal stability of PVC. These researches have prompted us to investigate in some depth the thermal properties of PVC-g-PSt by determining the rate of HCl evolution.

TABLE 1. Synthesis of PVC-g-PSt<sup>a</sup>

Styrene (M)	PVC (wt %)	Et <sub>2</sub> AlCl (M × 10 <sup>-2</sup> )	Time (min)	Temp. (°C)	Conversion (%)	GE (%)	PSt (%) <sup>b</sup>	Control (%)	Impact strength (ft-lb/in. of notch) <sup>c</sup>
Small-scale runs									
1.0	1.1	0.20	30	-30	0	-	-	0.3	
1.0	1.0	1.00	10	-30	7	41	16	4.9	
1.0	1.1	1.00	20	-30	12	24	16	0.3	
1.0	1.1	1.00	30	-30	48	9	28	0.3	
1.0	1.1	2.00	10	-30	79	5	26	0.3	
1.0	1.0	1.00	10	-15	19	13	14	4.9	
1.0	1.0	1.00	5	0	46	9	24	4.9	
1.0	3.0	1.00	30	-30	96	15	29	3.4	
2.0	3.0	1.00	5	-30	100	5	32	4.1	
Large-scale runs									
A	1.0	3.0	10	-30	13	26	4	4.8	0.8
B	1.0	3.0	10	-30	48	9	12	0.9	0.7
C	1.0	3.0	5	-30	96	10	23	4.1	0.6

<sup>a</sup>Solvent: 1,2-dichloroethane.<sup>b</sup>Determined by IR.<sup>c</sup>Impact strength of PVC: 1.0 ft-lb/in. of notch.

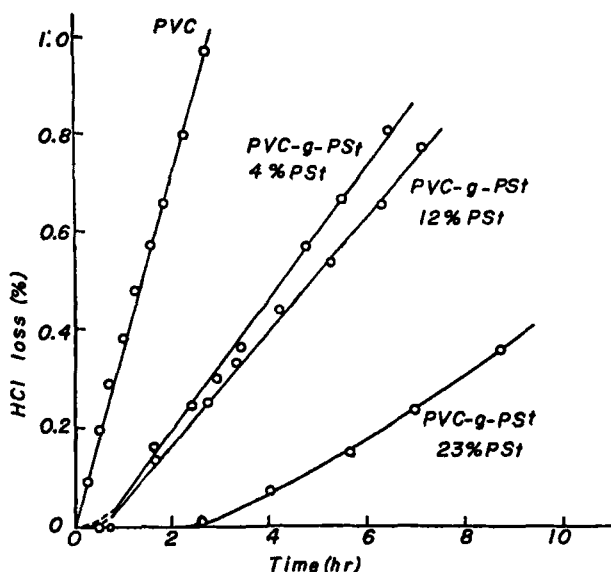


FIG. 1. Thermal dehydrochlorination of PVC-g-PSt ( $165^{\circ}\text{C}$  in  $\text{N}_2$ ).

Figure 1 shows the results of HCl evolution studies. The rate of HCl evolution was determined in a nitrogen atmosphere at  $165^{\circ}\text{C}$  [8]. HCl losses were normalized to original PVC content and compared to the thermal response of PVC backbone in the PVC-g-PSt. Evidently, increased amounts of PSt in the graft considerably enhance heat stability of the system. While HCl is liberated without an induction period from ungrafted PVC, even minor amounts of PSt branches delay the start of HCl evolution. The effect is quite remarkable with 23% PSt in the graft: Hardly any HCl evolution occurs even after 2.5 hr at  $165^{\circ}\text{C}$ .

The HCl evolution rate is also diminished with increasing PSt content. While the slope of the HCl loss versus time function is quite steep with virgin PVC, the slope is decreased by a factor of at least two in the presence of 4% PSt and many fold more with 23% PSt. Similar phenomena have been described and discussed with the PVC-g-polyisobutylene system [11, 14].

Evidently, the removal by grafting of "labile" allylic or tertiary chlorines in PVC and their replacement by more heat-stable C-C bonds, yields a less heat-sensitive product and delays the initiation of HCl evolution.

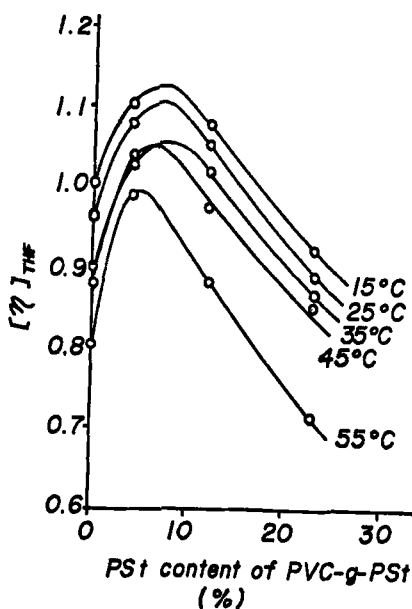


FIG. 2. Intrinsic viscosity of PVC-g-PSt.

### Intrinsic Viscosity Studies

The intrinsic viscosity of PVC-g-PSt samples of different overall compositions were determined as a function of temperature in the range from 15 to 55°C. Figure 2 is a plot of intrinsic viscosities as a function of graft PSt content at various temperatures. The  $[\eta]$  versus PSt content curves show maxima at 5-8% PSt at every temperature level. Similar unusual temperature effects on the intrinsic viscosity of graft have been published [15, 16], however a satisfactory explanation has yet to be developed. While their interpretation is still a matter of speculation, these phenomena are diagnostic for the presence of graft copolymer.

### Glass Transition Temperatures

The  $T_g$  of PVC-g-PSt was determined by dynamic measurements using a rheovibron. Figures 3 and 4 show the data. Significantly, dynamic modulus data clearly indicate the presence of only one  $T_g$ , i.e., only one phase, in the grafts.



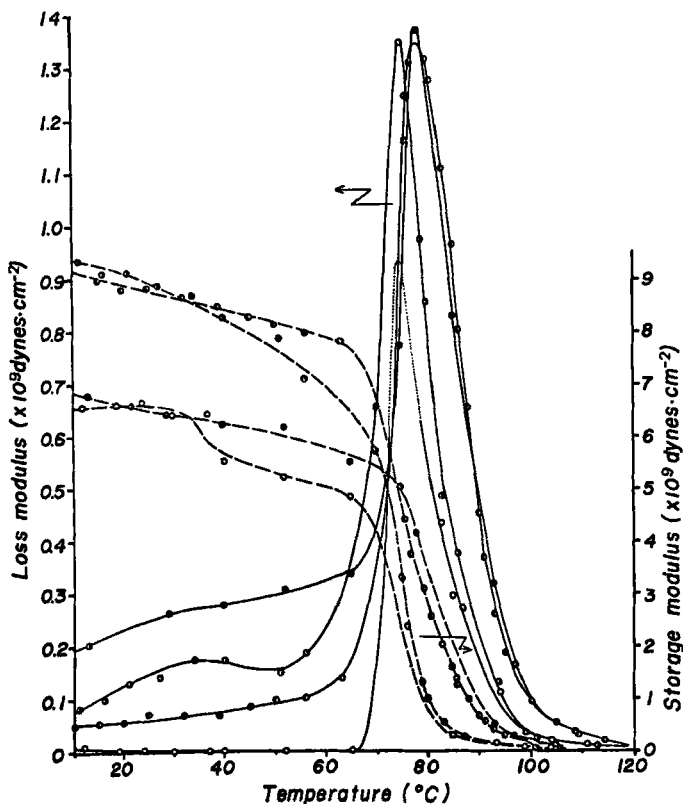


FIG. 3. Dynamic properties of PVC-g-PSt (Rheovibron, 3°C/min 110 cycles/min): (○) PVC; (◐) PVC-g-PSt (4% PSt); (◑) PVC-g-PSt (12% PSt); (●) PVC-g-PSt (23% PSt).

Extensive aggregation of PVC and PSt phases in PVC-g-PSt is also indicated by the homogeneity of THF solutions and optical clarity solution-cast films of our grafts. In contrast, solution cast films of PVC/PSt blends exhibit macroscopic phase separation and THF solutions of PVC/PSt blends separate into two layers. In these series of experiments, PVC/PSt blends were dissolved in THF in proportions of 96/4, 88/12, and 77/23 and the solvent slowly evaporated. Phase separation occurred at 9.6, 8.3 and 6.9 wt % blend in the solution, respectively.

In sum, these investigations directed toward the elucidation of the micromorphology of PVC-g-PSt leads us to conclude that grafts, at least up to ~23% PSt content, consist of one intimately aggregated,

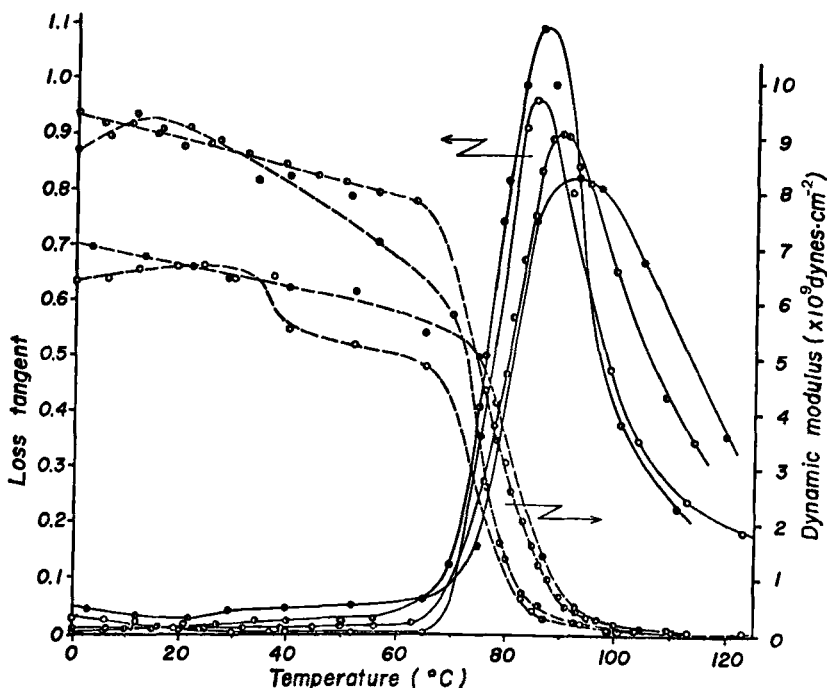


FIG. 4. Dynamic properties of PVC-g-PSt (Rheovibron,  $3^{\circ}\text{C}/\text{min}$ , 110 cycles/min): ( $\circ$ ) PVC; ( $\square$ ) PVC-g-PSt (4% PSt); ( $\triangle$ ) PVC-g-PSt (12% PSt); ( $\bullet$ ) PVC-g-PSt (23% PSt).

virtually homogeneous phase. That the chemical linking of two incompatible high polymers into one sequential copolymer may lead to intimate phase aggregation (one  $T_g$ ) has been observed previously in this laboratory [16] and by other workers [17, 18]. In the case of PVC-g-PSt, extensive phase compatibility is not too surprising, considering the proximity of solubility parameters of PVC ( $\delta = 9.4-10.8$ ) and PSt ( $\delta = 8.5-10.5$ ) [19].

### Physical-Mechanical Properties

Stress-strain response and impact properties of our grafts has been investigated. Figure 5 summarizes the stress-strain behavior of various PVC-g-PSt samples. The microdumbbells used for testing were initially clear and exhibited strong stress-whitening during extension. The data in Fig. 5 represent an average of five determinations.

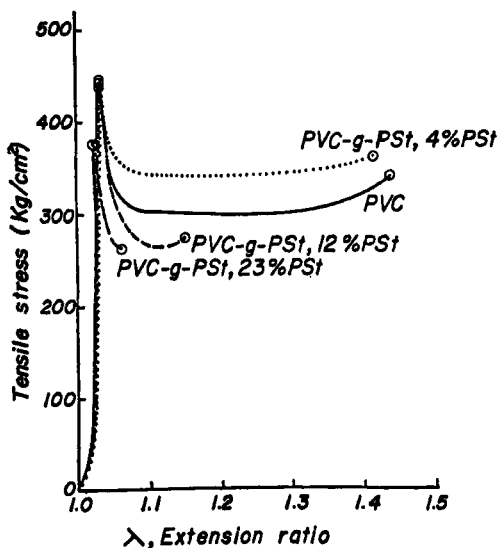


FIG. 5. Stress-strain behavior of PVC-g-PSt (Instron tester, strain rate 1 cm/min).

The ungrafted PVC and the grafts containing 4 and 12% PSt show the same yield point of  $\sim 450 \text{ kg/cm}^2$ , whereas that of the graft with 23% PSt is somewhat lower, with  $\sim 380 \text{ kg/cm}^2$ , all at an extension ratio  $\lambda \approx 1.03$ . Extension at failure decreases with PSt content.

The impact strengths of our PVC-g-PSt samples (cf. Table 1) were lower than that of the ungrafted PVC.

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