Dehydrochlorinated Poly(vinyl Chloride)-*g*-Polystyrene. II. Characterization and Physical Properties

A. K. MUKHERJEE and ACHLA GUPTA, *Department of Textile Technology, Indian Institute of Technology, Delhi, New Delhi 110016, India*

Synopsis

Dehydrochlorinated poly(vinyl chloride)-*g*-polystyrene (DHPVC-*g*-PSt) prepared by free radical grafting was characterized, and some of its physical properties were evaluated. The presence of graft was established by the appearance of new absorption peaks in the IR spectra of the graft copolymer. GPC analysis showed increase in the average molecular weights of the graft copolymer upon increase in the PSt content. Besides, GPC revealed the uniform PSt distribution of DHPVC-*g*-PSt. A marked improvement in the thermal stability of DHPVC-*g*-PSt over that of DHPVC and DHPVC/PSt blends was observed. Graft copolymers with high percent grafting were thermally more stable than even the original PVC. Stress–strain data indicated decrease in yield stress, breaking stress and elongation, along with an increase in the initial modulus, upon increase in PSt content of the graft copolymer.

INTRODUCTION

Graft copolymerization has proved to be a practical method of overcoming a number of the inadequate properties of poly(vinyl chloride) (PVC).[1–4] In PVC grafting, styrene is a widely used monomer. Poly(vinyl chloride)-*g*-polystyrene (PVC-*g*-PSt) graft copolymers have been studied using various techniques. Lechermeier et al.[5,6] carried out the gel permeation chromatography (GPC) analysis of anionically prepared PVC-*g*-PSt and observed that the elution volume of PVC after grafting is almost unchanged, the amount of homopolymer is large, and the PSt grafts are uniformly fixed on the PVC chains.

Kennedy and Nakao[7,8] studied the GPC chromatograms of cationically prepared graft copolymers and concluded that all the samples are highly homogeneous between elution counts 40 and 60, and the distribution shifts gradually towards low elution counts, i.e., high molecular weights, corresponding to the increase in PSt content.

Glass transition temperature (T_g) of PVC-*g*-PSt was determined using differential scanning calorimetry (DSC), differential thermal analysis (DTA), and Rheovibron. Thermal properties were observed by determining the rate of HCl evolution, and thermogravimetric analysis (TGA).[7]

Even though detailed investigations have been carried out on PVC-*g*-PSt, dehydrochlorinated poly(vinyl chloride)-*g*-polystyrene (DHPVC-*g*-PSt) remains uninvestigated. The present study is undertaken to characterize DHPVC-*g*-PSt and to evaluate some of the properties of the graft copolymer.

EXPERIMENTAL

Materials

Various DHPVC-*g*-PSt samples with different percent grafting were obtained by grafting DHPVC with styrene under different reaction conditions, as described earlier.[9]

Tetrahydrofuran (THF) was purified by refluxing over sodium borohydride and distilling from metallic sodium in nitrogen atmosphere. Double distilled THF was used for the chromatographic studies.

Characterization

Infrared Spectroscopy

Spectra were run on DHPVC-*g*-PSt films (cast from THF) using Unicam SP-1200 spectrophotometer in the range 4000–400 cm^{-1}.

Intrinsic Viscosity

Intrinsic viscosity [η] of the grafted samples was determined at 25°C, using an Ubbelohde viscometer. The samples were dissolved in peroxide-free THF (0.32%) under N_2 atmosphere. $\overline{M}_v$ (viscometry) of the graft copolymers were calculated from [η] values using a relationship proposed by Bohdanecky et al.[10] for PVC:

$$[\eta]_{THF}^{25°C} = 1.5 \times 10^{-4} M_w^{0.77} \, dL \cdot g^{-1}.$$

Gel Permeation Chromatography (GPC)

Waters Associates GPC Model 244 was used for the determination of average molecular weights ($\overline{M}_n$, $\overline{M}_v$, $\overline{M}_w$) and molecular weight distribution (MWD). The unit was operated with THF as carrier solvent at 25 ± 3°C using styragel columns with pore size of 10^4, 10^3, and 500 Å. A flow rate of 2 mL/min and a chart speed of 0.75 in./min was maintained in all experiments. The polymer concentration was 0.2% (w/v).

The concept of conventional calibration, i.e., a plot of the logarithm of molecular weight against elution volume, was used in the present study. The column combination was calibrated with the polystyrene standards of known molecular weights provided by Waters Associates. PSt calibration was converted to PVC calibration. For this, GPC analysis of PVC was carried out, and the $\overline{M}_v$ was calculated from its chromatogram and the PSt calibration. The $\overline{M}_v$ was also calculated from [η] value. The ratio of the $\overline{M}_v$ obtained by viscosity to that determined by GPC using PSt calibration was noted. The molecular weights of the standard PSt samples were multiplied by this ratio, and the new molecular weights thus obtained were used to plot the PVC calibration curve. The calibrations of gel-permeation chromatographic columns is shown in Table I and the calibration curves are presented in Figure 1.

The calibration curve of PVC was used for the DHPVC as well as the grafted samples.

TABLE I
Calibration of Gel-Permeation Chromatographic Columns

PSt calibration		PVC calibration			
Molecular weight ($\overline{M}_w \times 10^{-3}$)	Peak elution volume (mL)	$\overline{M}_v \times 10^{-3}$ (viscometry)	$\overline{M}_v \times 10^{-3}$ (GPC) using PSt calibration	$\overline{M}_v$ (viscometry)/ $\overline{M}_v$ (GPC)	$\overline{M}_w \times 10^{-3}$ (for PVC calibration)
200.0	17.1				300.0
110.0	18.0				165.0
		92.5	59.8	1.5	
35.0	19.7				52.5
3.6	23.8				5.4

Properties

Thermal Properties

Thermogravimetric Analysis: Thermogravimetric analysis was carried out on Stanton Redcroft TG-750 Thermobalance in nitrogen atmosphere. The samples were heated at a uniform heating rate of 10°C/min from room temper-
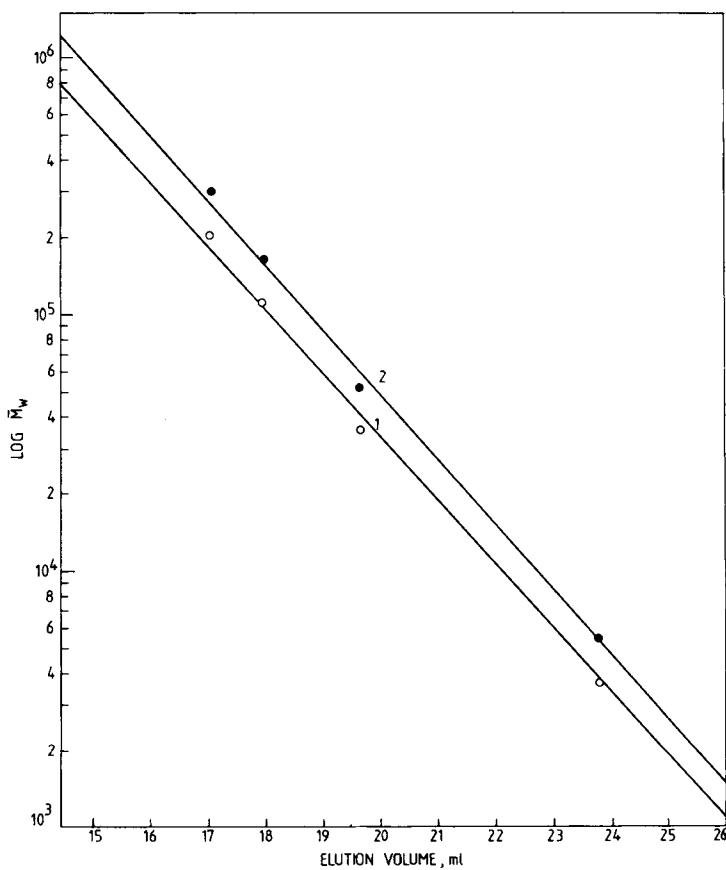

Fig. 1. GPC calibration curves of (1) PSt and (2) PVC.

ature to 800°C. Primary thermograms were obtained by plotting residual weight against temperature. From the thermograms, initial decomposition temperature (IDT), and integral procedural decomposition temperature (IPDT) were calculated. IPDT was calculated over the temperature range 100–500°C.

Differential Thermal Analysis: Differential thermal analysis was carried out using a Stanton Redcroft DTA 673-4 instrument with alumina as reference, in vacuum. The samples were heated from room temperature to 450°C at a heating rate of 10°C/min.

Color Development Studies: Color development studies were carried out using electrothermal melting point apparatus at a heating rate of 5°C/min.

Mechanical Properties

Stress–strain behavior was determined using a tensile tester—Instron—at 25°C/65% RH and microdumbbells die cut from films cast from 2% solutions in THF.

In determining the tensile properties, 10 samples were tested for each experiment. Each quoted result represents the mean value obtained from 10 tests. A standad deviation is also attached with the tensile data.

The load elongation curves were obtained using the following setting on Instron: gauge length = 2 cm, crosshead speed = 0.5 cm/min, and chart speed = 20 cm/min on a full scale load of 2 kg. From the curves, the yield stress, breaking stress, elongation at break, and initial modulus were calculated.

RESULTS AND DISCUSSION

Infrared Spectroscopy

Infrared (IR) spectroscopy was used to ascertain the presence of polystyrene in the composition of the graft copolymers. Figure 2 shows the IR spectra of PVC, DHPVC, and DHPVC-*g*-PSt samples with 11.4%, 22%, and 40% grafting. All the absorption bands similar to those of DHPVC[11] were observed in the absorption spectra of the graft copolymers. A few new peaks also appeared in the spectra of DHPVC-*g*-PSt. These are as follows:

Absorption band (cm^{-1})	Assignment
3070, 3040	Aromatic C—H stretching
1610	In-plane bend-stretching vibrations of phenyl ring
760	Out of plane hydrogen deformation

The appearance of new absorption peaks in the IR spectra of DHPVC-*g*-PSt clearly indicates that styrene has been incorporated in the DHPVC backbone.

Intrinsic Viscosity

Intrinsic viscosities of DHPVC-*g*-PSt samples of different PSt contents were determined in THF solutions. The results are presented in Table II. Figures
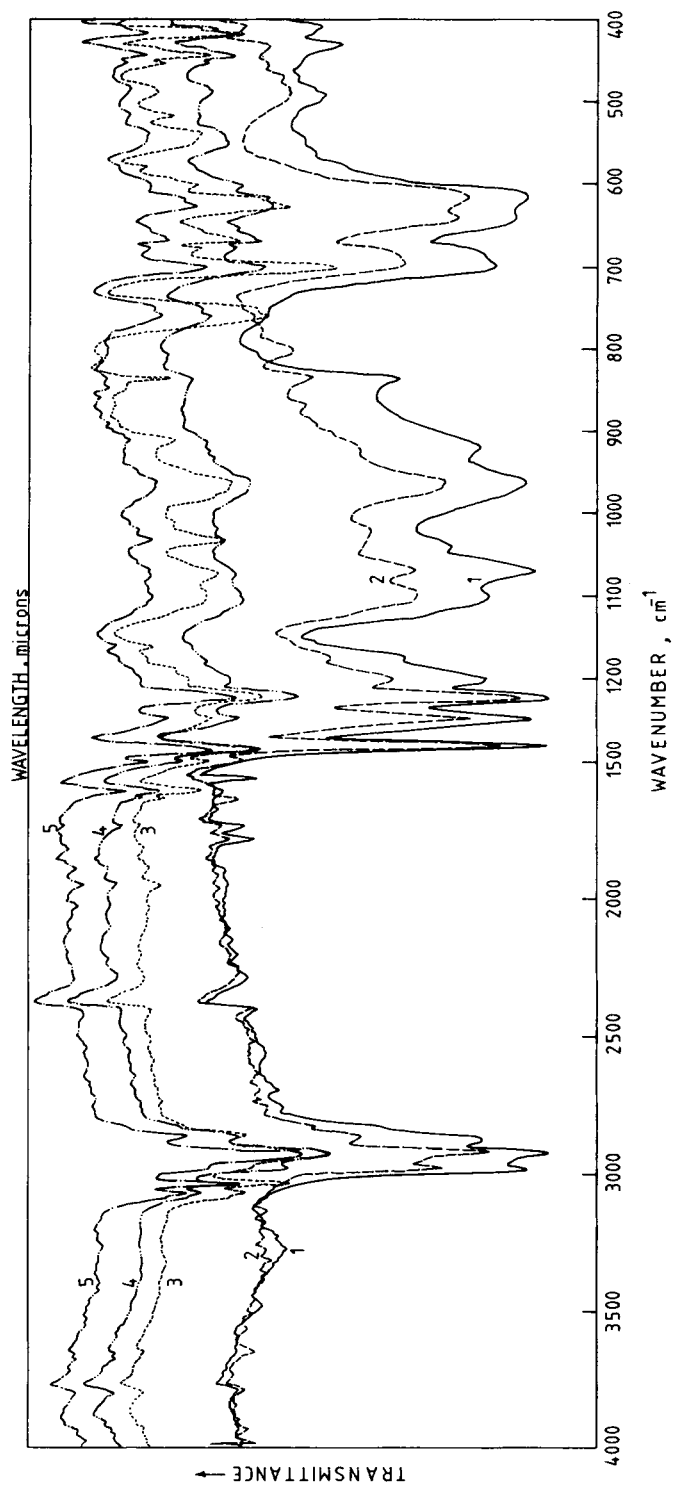
Fig. 2. IR spectra of films cast from THF solutions of (1) PVC, (2) DHPVC, and DHPVC-*g*-PSt samples with (3) 11.4% PSt, (4) 22.0% PSt, and (5) 40.0% PSt.
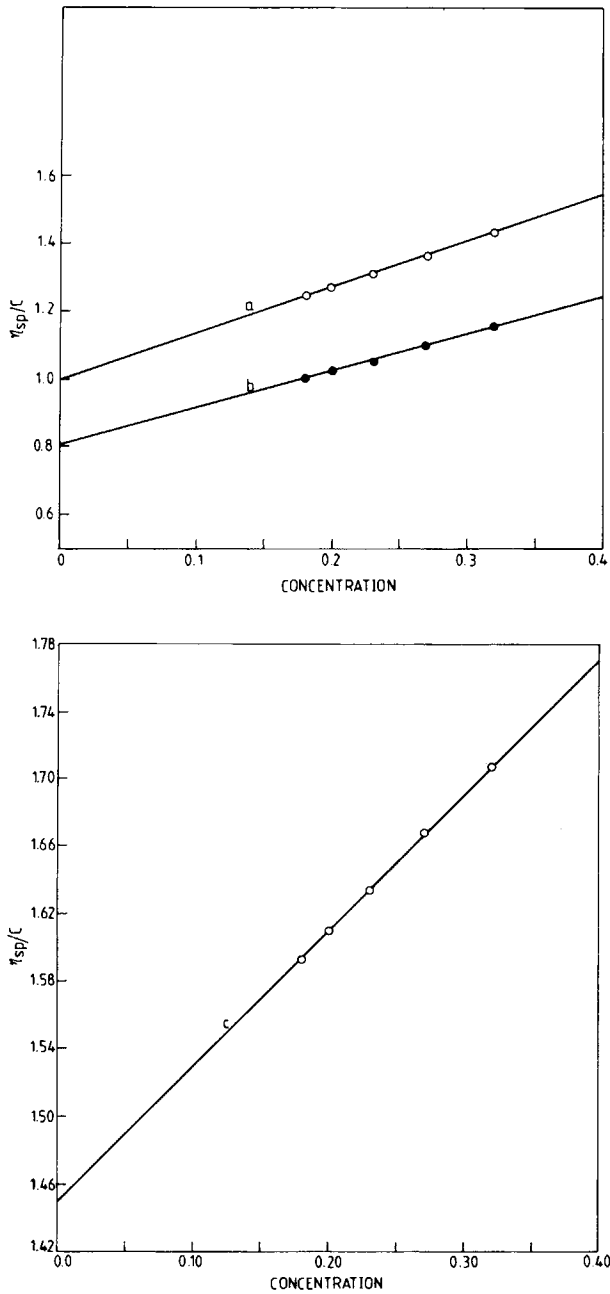
Fig. 3. Linear extrapolation of viscosity data (concentration, g/dL): (a) PVC, (b) PVC dehy-drochlorinated in pyridine (41.7 g·L^{-1}) at 120°C for 135 min; linear extrapolation of viscosity data: (c) DHPVC-g-PSt with 4% PSt; linear extrapolation of viscosity data: (d) DHPVC-g-PSt with 5.4% PSt; linear extrapolation of viscosity data: DHPVC-g-PSt with (e) 22% PSt, (f) 32.6% PSt, and (g) 47% PSt.

3(a)–(g) show a linear extrapolation of viscosity data. Changes in $[\eta]$ with percent grafting are presented in Figure 4.

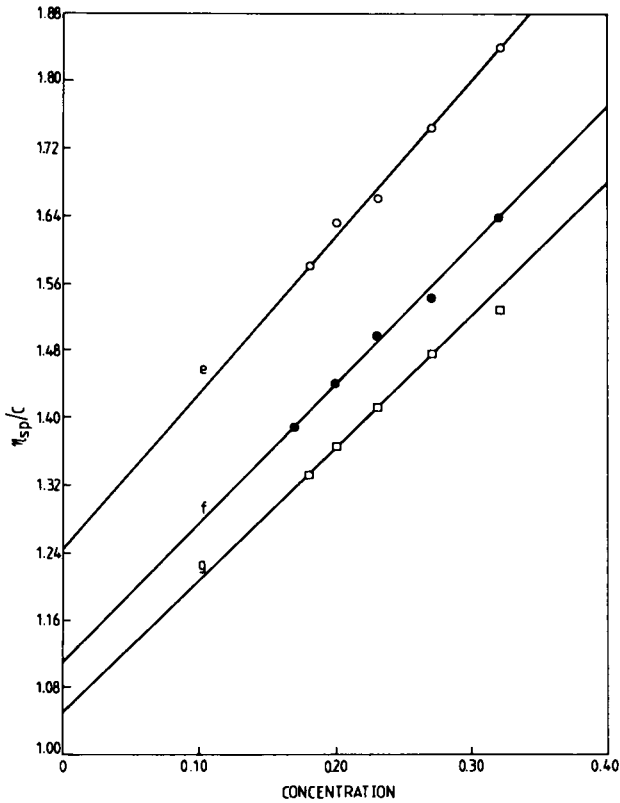The intrinsic viscosity increases on increasing the percent grafting and reaches
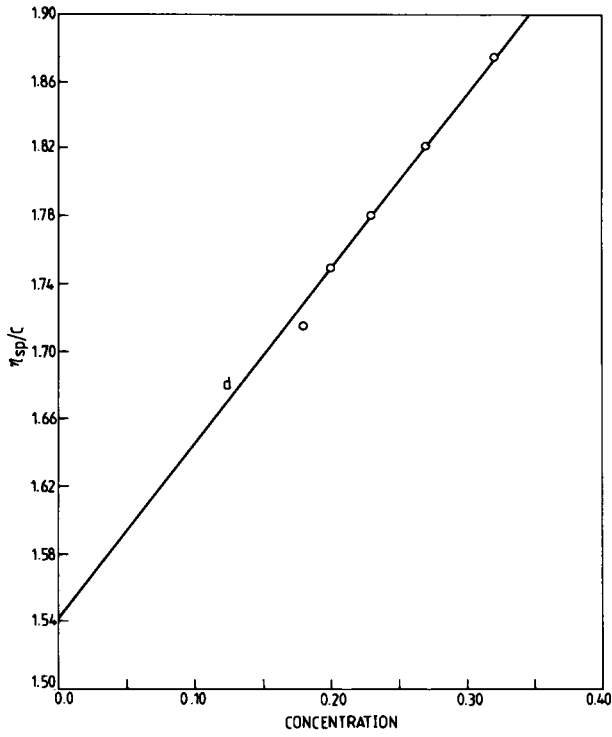
Fig. 3. (*Continued from the previous page.*)

TABLE II
Effect of Percent Grafting on Intrinsic Viscosity and Average Molecular Weights of DHPVC-g-PSt

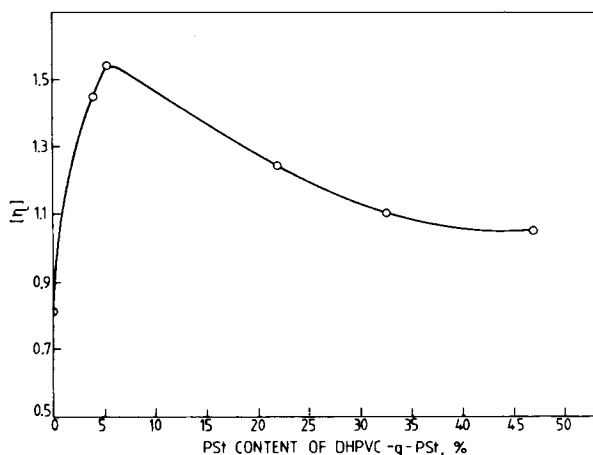| Sample no.	PSt in DHPVC-g-PSt (%)	$[\eta]$ dL·g^{-1}	Slope (η_{sp}/C vs. C)	k' (Huggins constant)	$\overline{M}_v \times 10^{-3}$ (Viscometry)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{M}_v \times 10^{-3}$ (GPC)	$\overline{M}_w \times 10^{-3}$ (GPC)	H ($\overline{M}_w/\overline{M}_n$)
PVC	—	1.00	0.34	0.34	92.5	43.4	83.9	96.5	2.2
DHPVC	—	0.81	0.28	0.42	70.3	37.9	92.8	109.3	2.8
A$_2$	4.0	1.45	1.00	0.48	149.8	73.0	135.5	156.5	2.1
B$_3$	5.4	1.54	1.30	0.55	162.0	—	—	—	—
A$_4$	22.0	1.24	1.18	0.77	122.3	73.0	146.3	170.1	2.3
D$_2$	32.6	1.10	1.05	0.87	104.7	74.1	162.7	191.1	2.5
B$_2$	47.0	1.05	0.98	0.89	98.5	83.5	167.1	195.7	2.3

Fig. 4. Effect of percent grafting on intrinsic viscosity [η] (dL/g) of DHPVC-*g*-PSt.

a maximum value at 5.4% grafting, beyond which there is a significant decrease in [η]. The $\overline{M}_v$ calculated from viscosity data follow a similar trend.

The reduced viscosity (η_{sp}/C) of the polymer solution is expressed by the Huggins equation:

$$\eta_{sp}/C = [\eta] + k'[\eta]^2 C$$

k', which is a measure of the polymer–solvent interaction, is obtained from the slope of the η_{sp}/C vs. C plots ($k' = \text{slope}/[\eta]^2$).

Figures 3(a)–(g) and Table II show that the slope of η_{sp}/C vs. C plots increases with percent grafting, reaches a maximum value at 5.4% grafting, and then decreases with further increase in percent grafting. However, the k' values increase continuously with increase in percent grafting. The increase in k' values reflects a decrease in the polymer–solvent interaction.[12,13] This may be due to an increase in stiffness of the polymer chains by the incorporation of bulky PSt side chains. The decrease in the polymer–solvent interaction would reduce the hydrodynamic volume, and hence there should be a decrease in [η] of the graft copolymer. On the contrary, there is an increase in the [η] of DHPVC-*g*-PSt. This continues, however, only up to 5.4% grafting, and on further increasing the percent grafting there is a decrease in the [η].

Probably, the DHPVC is not fully extended in THF and when a small amount of incompatible PSt is grafted to it, the DHPVC chains will try to avoid contact with the "intruder" by extending as much as possible; hence the hydrodynamic volume will dilate, and the [η] will increase. However, with the continued introduction of PSt branches and/or increase of PSt branch molecular weights the DHPVC chains soon become fully extended and the hydrodynamic volume increase stops. This happens perhaps at 5.4% grafting. Beyond this, the effect of decreasing the polymer–solvent interaction with increasing percent grafting dominates which leads to a reduction in the overall hydrodynamic volume and hence a decrease in [η] of the graft copolymer (Fig. 4).

Thus, it can be concluded that with the change in the extent of grafting the magnitude of the polymer–solvent interaction undergoes change, and as a result there is a change in the hydrodynamic volume. This requires different values for the constants in the Mark–Houwink equation [η] = KM^α in determining the

molecular weights of different grafted samples from [η] values. In the present
investigation the Mark–Houwink constants (K and α) of PVC were used also
for the grafted samples. This is due to the difficulty in determining the K and
α values of DHPVC as well as the graft copolymers. Therefore, the determi-
nation of $\overline{M}_v$ from viscosity data does not give the absolute molecular weights
but provides only a relative study of the changes in the molecular weight.

Gel-Permeation Chromatography

The GPC distribution curves of PVC, DHPVC, and DHPVC-g-PSt samples
are presented in Figure 5, and the calculated average molecular weights ($\overline{M}_n$,
$\overline{M}_v$, and $\overline{M}_w$) are given in Table II. GPC distribution curves of all the graft co-
polymers were smooth and monomodal. This shows the uniform PSt distribu-
tion in the composition of the graft copolymers.

A low molecular weight tail appeared in the GPC distribution curve of DHPVC.
This may be due to the decrease in the polymer–solvent interaction caused by
the stiffening effect of long conjugated polyenes present in the polymer. De-
crease in the polymer–solvent interaction reduces the hydrodynamic volume,
and this leads to the development of a low molecular weight tail in the distri-
bution curve. On incorporating 4% PSt to the DHPVC, hydrodynamic volume
shows an increase. Molecular weight also increases. This shifts the distribution
towards high molecular weight. Calculated average molecular weights also show
an increase. On increasing the percent grafting (22%) the hydrodynamic volume
shows a decrease, and this is reflected in an increase in the length of the low
molecular weight tail in the distribution curve. This effect continues with further
increase in percent grafting. However, the increase in the molecular weight with
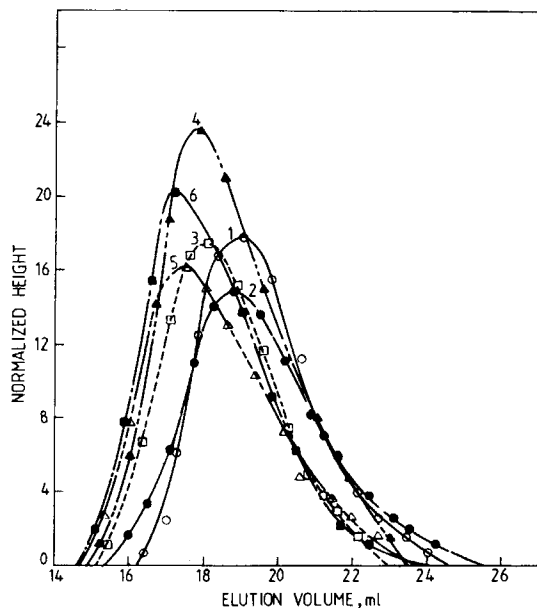percent grafting shifts the GPC curves continuously towards high molecular

Fig. 5. GPC curves of (1) PVC, (2) DHPVC, and DHPVC-g-PSt samples with (3) 4.0% PSt, (4)
22.0% PSt, (5) 32.6% PSt, (6) 47.0% PSt.

weight (Fig. 5). This results in a continuous increase in the average molecular weights (Table II).

In the GPC analysis, the calibration curve of PVC was used for the grafted samples also. So the results of GPC analysis give only a semiquantitative measure of the molecular weights of the graft copolymers, not the absolute molecular weights.

Both viscosity and GPC are thus relative methods only and are used for simple relative comparison among the grafted samples.

On comparing the results obtained from viscosity measurements with those from GPC analyses, it appears that there is a great difference in $\overline{M}_v$ (viscometry) and $\overline{M}_v$ (GPC). This may be due to the fact that the theoretical understanding of viscosity method is lacking due to the complexity in various parameters involved in the method.

Thermal Analysis

Thermogravimetric Analysis

Thermal properties of DHPVC-*g*-PSt were determined mainly by TGA studies. Primary thermograms of PVC, DHPVC, and DHPVC-*g*-PSt samples are presented in Figure 6, those of DHPVC/PSt blends in Figure 7, and the corresponding thermal data in Table III.
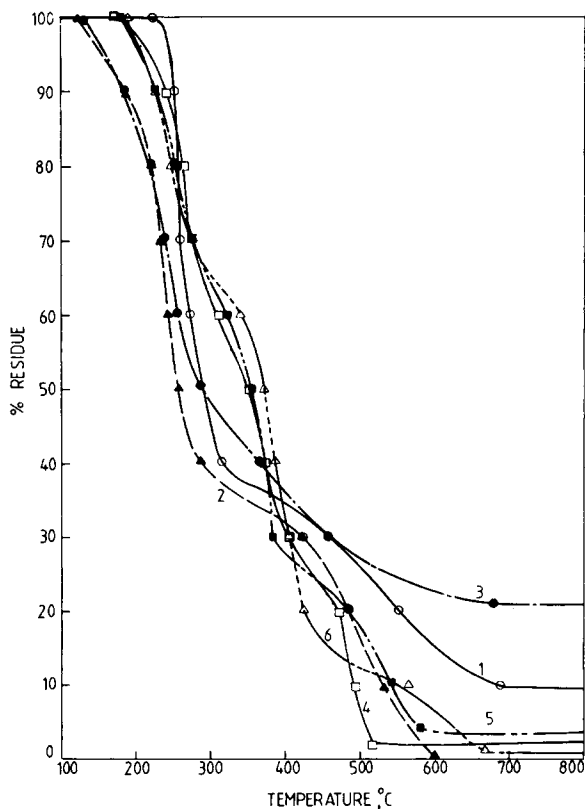

Fig. 6. Primary thermograms of (1) PVC, (2) DHPVC, and DHPVC-*g*-PSt samples with (3) 5.4% PSt, (4) 22.0% PSt, (5) 40.0% PSt, and (6) 47.0% PSt.
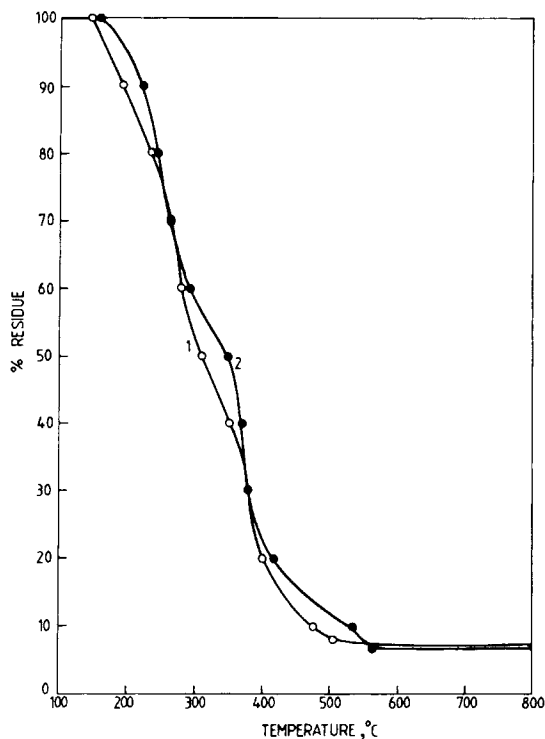
Fig. 7. Primary thermograms of DHPVC/PSt blends with composition (by weight): (1) 78/22; (2) 60/40.

DHPVC shows a two step thermal decomposition pattern similar to that of PVC, except for a decrease in thermal stability.[14] The two-step thermal decomposition pattern of DHPVC disappears in the DHPVC-g-PSt, as the percent grafting increases (Fig. 6).

IDT and IPDT also show a continuous increase corresponding to the increase

TABLE III

Thermogravimetric Analysis of PVC, DHPVC, DHPVC-g-PSt Samples, and DHPVC/PSt Blends[a]

Sample no.	PSt in DHPVC-g-PSt (%)	IDT (°C)	T_{50} (°C)	IPDT (°C)
PVC	—	235	290	346
DHPVC	—	120	259	315
B$_3$	5.4	127	285	330
A$_4$	22.0	170	346	349
DHPVC/PSt blend (78/22)	—	146	311	320
C$_3$	40.0	176	351	350
DHPVC/PSt blend (60/40)	—	158	351	340
B$_2$	47.0	187	371	351

[a] DHPVC/PSt blends were prepared by taking each component by weight.

in percent grafting (Table III), thus indicating an improvement in thermal sta-
bility of the graft copolymer as compared to DHPVC. Thermal stability im-
provement was remarkable in the range 245–345°C. The graft copolymer with
47% grafting showed thermal stability improvement over PVC too (Table
III).

It can be seen from Figure 7 and Table III that the graft copolymers have
higher thermal stability than that of the blends of similar composition. For
example, DHPVC-*g*-PSt samples having 22% and 40% grafting showed higher
IDT and IPDT than DHPVC/PSt blends with 78/22 and 60/40 composition,
respectively.

The thermograms of DHPVC, DHPVC-*g*-PSt samples, and DHPVC/PSt
blends (in equal wt % as the two components present in the grafted samples),
showed completely different and independent behavior. This also confirms the
contention that the grafting technique used in the present study has produced
grafted products, not the physical blends of DHPVC and PSt.

Differential Thermal Analysis

DTA technique was also used to evaluate the thermal properties of
DHPVC-*g*-PSt. DTA thermograms of PVC, DHPVC and the grafted samples
are shown in Figure 8.

In DTA scan of PVC there was no clear T_g, but only a broad shift in base line
was observed in the range of 70–80°C. DTA thermogram of DHPVC showed
T_g in the same range.[14] However, in the case of DHPVC-*g*-PSt the broad shift
was observed between 75–85°C, indicating that the polymer is a graft, not a blend,
and also showing the increase in T_g upon grafting.

A DTA thermogram of PVC also showed a sharp endothermic degradation
peak having a maximum at 270°C. The endothermic peak shift towards lower
temperature (peak maximum at 155°C) in DHPVC.[14] In DHPVC-*g*-PSt, the
degradation peak shifted towards higher temperature. Thus, the improvement
in thermal stability of DHPVC-*g*-PSt over PVC and DHPVC as observed by
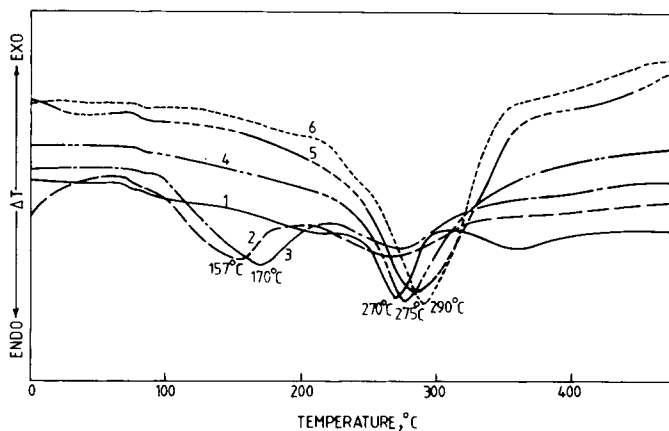TGA has been corroborated by DTA.

Fig. 8. DTA thermograms of (1) PVC, (2) DHPVC, and DHPVC-*g*-PSt samples with (3) 5.4%
PSt, (4) 22.0% PSt, (5) 40.0% PSt, and (6) 47.0% PSt.

Color Development Studies

Color development studies were carried out to observe the difference between the thermal stability of DHPVC-g-PSt and DHPVC at low extent of heat degradation. The discoloration of PVC, DHPVC, and DHPVC-g-PSt samples, corresponding to the increase in temperature is as follows:

	Temperature (°C) at the occurrence of colors				
	Pink	Orange	Red	Brown	Black
PVC (colorless)	180	220	250	280	300
DHPVC (pink)	—	—	140	160	260
DHPVC-g-PSt (22% PSt, light violet)	—	—	150	180	280
DHPVC-g-PSt (40% PSt, violet)	—	—	160	190	280

These results indicate improvement in the thermal stability of DHPVC-g-PSt over DHPVC in the early stages of heat degradation.

Mechanical Properties

Mechanical properties of DHPVC-g-PSt films are illustrated by stress–strain curves shown in Figure 9, and are tabulated in Table IV. A decrease in yield stress, breaking stress and elongation, together with an increase in initial modulus, was observed corresponding to the increase in PSt content of the graft copolymer.

Increase in the initial modulus shows that the stiffness increases with grafting. This is due to the bulky PSt side chains. As PSt is a glassy polymer, its incor-
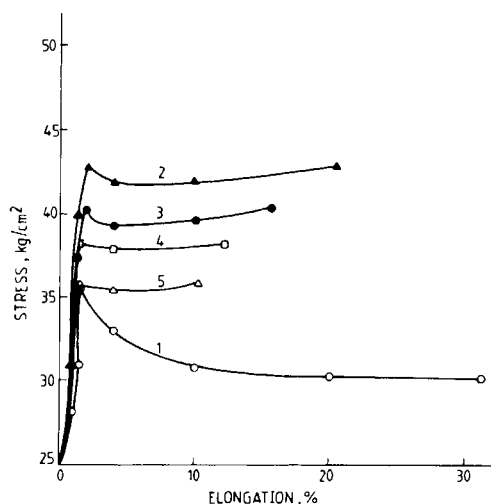

Fig. 9. Stress–Strain behavior of (1) PVC, (2) DHPVC, and DHPVC-g-PSt samples with (3) 4.0% PSt, (4) 22.0% PSt, and (5) 40.5% PSt.

TABLE IV
Mechanical Properties of PVC, DHPVC, and DHPVC-*g*-PSt Samples

Sample no.	PSt in DHPVC-*g*-PSt (%)	Maximum yield stress (kg/cm^2)	Yield strain (%)	Initial modulus (kg/cm^2)	Breaking stress (kg/cm^2)	Elongation at break (%)
PVC	—	35.6(±1.5)	2.64(±0.13)	1350(±21.4)	30.2(±2.2)	31.2(±2.6)
DHPVC	—	42.9(±1.7)	2.08(±0.08)	2050(±17.0)	43.0(±2.0)	20.3(±1.4)
A$_2$	4.0	40.3(±0.6)	1.88(±0.03)	2146(±19.5)	40.5(±0.7)	15.6(±0.4)
A$_4$	22.0	38.2(±0.6)	1.67(±0.03)	2293(±20.0)	38.3(±0.5)	12.2(±0.4)
C$_2$	40.5	35.8(±1.1)	1.52(±0.05)	2363(±21.4)	35.9(±0.8)	10.2(±0.3)

poration into the PVC chains increases the brittleness of the polymer. This is reflected in the continuous decrease in breaking elongation with increasing percent grafting.

References

1. N. G. Gaylord and A. Takahashi, *J. Polym. Sci. B, Polym. Lett.*, **8**, 361 (1970).
2. B. X. Plastics Ltd. (Great Britain), Fr. Pat. 1,333,311 (1962).
3. J. M. Heaps, J. E. Bramfitt, and R. R. Smith to B. X. Plastics Ltd., Br. Pat., 1,017,533 (1961).
4. Solvay et Cie., Belg. Pat. 673,317 (1965).
5. G. Lechermeier, C. Pillot, J. Gole, and A. Revillon, *J. Appl. Polym. Sci.*, **19**, 1979 (1975).
6. G. Lechermeier, A. Revillon, and C. Pillot, *J. Appl. Polym. Sci.*, **19**, 1989 (1975).
7. J. P. Kennedy and M. Nakao, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **30**, 73 (1977).
8. J. P. Kennedy and M. Nakao, *J. Macromol. Sci. Chem.*, **A12**(2), 197 (1978).
9. A. K. Mukherjee and Achla Gupta, *J. Appl. Polym. Sci.*, to appear.
10. M. Bohdanecky, K. Solc, P. Kratochvil, M. Kolinsky, M. Ryska, and D. Lim, *J. Polym. Sci.*, *A-2*, **5**, 343 (1967).
11. A. K. Mukherjee and Achla Gupta, *J. Macromol. Sci. Chem.*, **A16**(6), 1161 (1981).
12. Ch'en Jun-Shih and Ch'ien Jèn-Yüan, *Gaofyntszy Tunsyun*, **1**, 130 (1957).
13. G. C. Berry, *J. Chem. Phys.*, **46**, 1338 (1967).
14. A. K. Mukherjee and Achla Gupta, *J. Macromol. Sci. Chem.*, **A16**(7), 1323 (1981).