

Anionic Graft Copolymers. I. Poly(vinyl Chloride)-g-Polystyrene. Preparation and Characterization

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Synopsis

Graft copolymers of PVC-g-PS of controlled branching were prepared by carbanionic deactivation. The reaction products were characterized mainly by GPC. It appears that secondary reactions affect the efficiency of the grafting, chiefly at low ratios of polystyrene to poly(vinyl chloride). Techniques of grafting and analyses are discussed.

INTRODUCTION

The authors have been engaged for some time in the synthesis of graft copolymers of well-defined structures. We have considered both free-radical and ionic methods, as reviewed by Rempp,¹⁻⁴ and have opted for a grafting technique involving an anionic process. Specifically, we have chosen to graft polystyrene (PS) formed by the "living polymer" technique,⁵ and still bearing its conjugate cation, onto well-characterized poly(vinyl chloride) (PVC). The main advantages of this anionic path⁶ are that it allows discrete characterization of the backbone and the grafts, and thus allows a choice of chain lengths in each case and that it permits one to prepare copolymers of high molecular weight with relative ease. The latter is due to the large number of reactive sites, the C—Cl bonds, on the backbone polymer, PVC.

In order to have reasonable experimental conditions, i.e., viscosity, concentration, number of sites, reactivity, and possibility of characterization, we have used a commercial PVC of $\bar{M}_n = 33,000$, and a lower molecular weight PS, $\bar{M}_n = 5$ to 10,000, so that it was possible to obtain fairly high molecular weight copolymer with a good PS/PVC ratio. The efficiency of grafting may be expressed either by the ratio of reacted chain number PS per chain of PVC or by the per cent of the reacted Cl on the backbone.

For a good knowledge of the process, an accurate method of characterization is necessary. To this end, GPC has been found valuable, mainly with the help of two detectors.⁷ Because there is only slight change of the elution volume at low grafting ratios, the different responses of a differential refractometer and a UV photometer (no UV response of PVC) allow the exact determination of the composition and calculation⁸ of the MW using the PS or PVC calibration.

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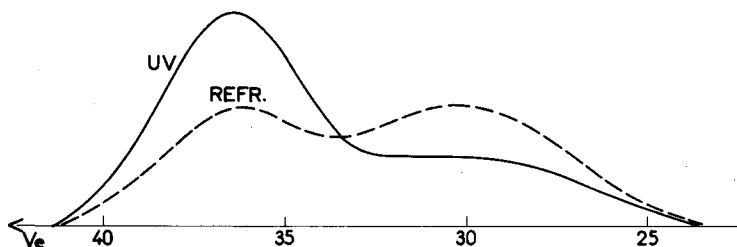


Fig. 1. UV and refractometric (REFR) chromatograms of product 6.

The first GPC analyses show bimodal chromatograms with a small amount of grafted PS (Fig. 1). Before osmometric measurement, and in order to make a comparison between direct methods (synthesis, UV spectroscopy, osmometry) and GPC, the product was fractionated to eliminate these materials of low PS content. After decomposition of the GPC curve, knowing the peaks of PS and initial PVC, a good agreement between all the methods was obtained.

EXPERIMENTAL

Reagents

These were purified as previously described.⁹

Synthesis

Living polystyrene was reacted with PVC at low temperatures to reduce the secondary reactions. The following was a typical experiment:

Synthesis Under Vacuum of the Graft Fragment. Into 400 ml THF, 10 ml *n*-BuLi (Fluka) in hexane (0.10 Ml^{-1}) is poured, and immediately (to limit the extent of reaction between *n*-BuLi and THF), 8 g of styrene is added by distillation. The reactor was thermostated at -60°C and the mixture was stirred for 1 hr.

Grafting. The above solution was slowly poured into 400 ml THF solution containing 2% of a commercial PVC (Rhône-Progil, mass process), and the grafting reaction was allowed to proceed for 15 min. This solution was mixed with CH_3OH and the precipitated polymer was dried under vacuum at room temperature to a constant weight. From the weight of the recovered sample, the yield of the reactions was calculated.

Characterization

The PS content was measured by UV absorption (static UV) at 260 nm with a Cary spectrophotometer, in THF solvent. The cell length was 1 mm, and calibration was made using pure PS. The ϵ found was $2 \text{ l. g}^{-1} \text{ cm}^{-1}$.

A Melab membrane osmometer with ortho-dichlorobenzene at 60°C was used for \bar{M}_n determinations of both whole mixtures and fractions.

The fractionations were made using THF as solvent and C_6H_6 as precipitant. C_6H_{12} gave a better separation of the PS. In fact, the high dispersity of the PVC and the distribution of grafting made difficult a complete separation of homopolystyrene and copolymer.

Classical GPC equipment was used with THF solvent (flow rate 1.1 ml min^{-1}) at 25°C , four columns ($1.3 \text{ m} \times 0.8 \text{ cm}$) filled with porous silica spheres (Spherosil

XOA400, XOB020, XOB075) and two detectors on line, a differential refractometer (Waters R 4), and a double-beam UV spectrometer (Chromatronix) at $\lambda = 254$ nm.

Interpretation of Chromatograms

S and S' are, respectively, the refractometric and UV responses of the PS, and C is the refractometric response of the PVC (no UV absorption), representing the peak area for 1 g of the polymer. For a mixture of PS and PVC, x is the weight fraction of PS. Thus,

$$\begin{aligned} A \text{ (refractometric peak area)} &= xS + (1 - x) C \\ A' \text{ (UV peak area)} &= xS'. \end{aligned}$$

Then,

$$A/A' = S/S' + (1 - x) C/xS'$$

where $S/S' = 0.58$, $C/S' = 0.3$, and $C/S = 0.52$. The value of x is

$$x = 0.3 / ((A/A') - 0.28) \quad (1)$$

taking into account the two chromatograms. From one chromatogram, it is possible to get x :

$$x = (A + C) / (S - C) \quad (2)$$

or

$$x = A'/S'. \quad (3)$$

In formula (1), the ratio A/A' was used, thus eliminating errors in the weight of sample. This value of x is insufficient to determine the extent of grafting since the chromatograms are bimodal, representing mixtures of copolymer and unreacted PS.

The chromatograms of pure PS indicate that the second peak for the mixture in the low MW region is due to this unreacted PS, so a decomposition of the peak must be done first, for instance, with the help of a "curve analyzer" (du Pont). From the UV curve (that is, the PS component), by punctual transformation $S/S' = 0.58$, it is possible to determine the PS refractometric curve S_R in Figure 2. This S_R curve is then decomposed in the two constituents, unreacted (h-PS) and grafted (g-PS). From the difference between the S_R curve and the one observed, the contribution of PVC can be found.

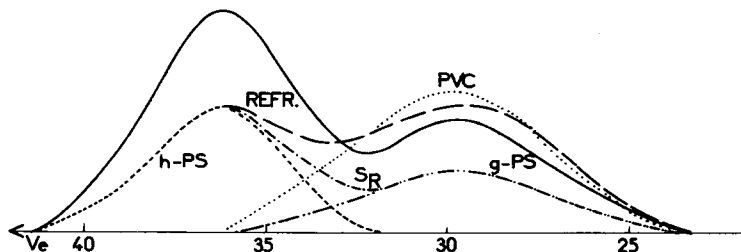


Fig. 2. UV and refractometric (REFR) chromatograms of product 8 and PVC. Derived refractometric trace (S_R) of the PS-constituent and decomposition in homo PS (hPS) and graft PS (g-PS).

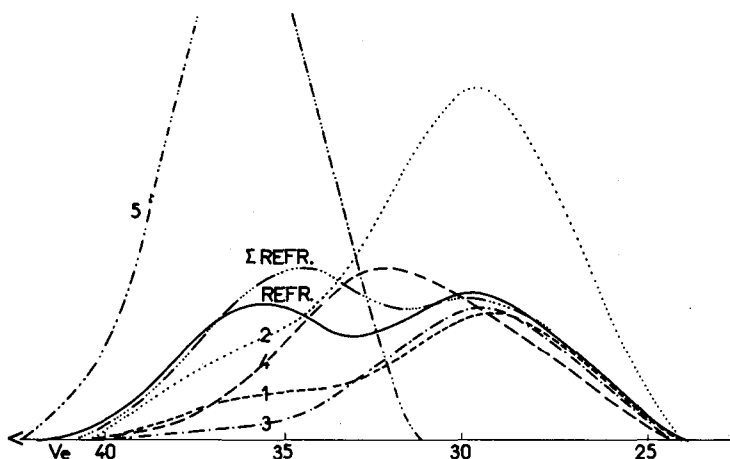


Fig. 3. Refractometric chromatograms of product 8 and of its fractions. Recomposed chromatogram of the mixture.

From the areas of these curves, the three quantities amount of homo PS x_1 , reacted PS $(x - x_1)$, and PVC $(1 - x)$ are determined, corresponding to the following equations:

$$A = x_1 S + (x - x_1) S + (1 - x) C$$

$$A' = x_1 S' + (x - x_1) S'.$$

Since the $\bar{M}_{n(\text{PS})}$ and $\bar{M}_{n(\text{PVC})}$ of the two constituent polymers are known, the number of the chains is

$$(x - x_1)/\bar{M}_{n(\text{PS})} \text{ grafted to } (1 - x)/\bar{M}_{n(\text{PVC})}$$

and the average grafting ratio is

$$\bar{l} = \frac{x - x_1}{1 - x} \frac{\bar{M}_{n(\text{PVC})}}{\bar{M}_{n(\text{PS})}}.$$

The theoretical ratio \bar{l}' is

$$\bar{l}' = \frac{x}{1 - x} \frac{\bar{M}_{n(\text{PVC})}}{\bar{M}_{n(\text{PS})}}.$$

determined either by chromatography or spectroscopy or from the experimental conditions of the synthesis.

The method can be applied to the whole mixture and to the fractions, but it is not possible to determine \bar{l} for the fractions since the \bar{M}_n of the PVC cuts is not known. From the weight of the fractions and their composition, it is possible to redetermine the chromatogram of the compound (Fig. 3).

From the value of \bar{l} , it is possible to calculate the true \bar{M}_n of the copolymer:

$$\bar{M}_{n(\text{copo})} = \bar{M}_{n(\text{PVC})} + \bar{l} \bar{M}_{n(\text{PS})}.$$

The comparison with the \bar{M}_n measured directly by osmometry is only possible if the homo PS is carefully eliminated. If not, one obtains

$$\bar{M}_{n(\text{mixture})} = \frac{\bar{M}_{n(\text{copo})} \frac{1 - x}{\bar{M}_{n(\text{PVC})}} + x_1}{\frac{1 - x}{\bar{M}_{n(\text{PVC})}} + \frac{x_1}{\bar{M}_{n(\text{PS})}}}.$$

It is to be noted that \bar{l} is an average value for the complete copolymer since it is impossible to distinguish ungrafted and grafted PVC and determine the distribution of the grafts. A simpler method to obtain \bar{l} , without decomposition, when the peaks of PVC and PS are distinct is to use the instantaneous heights of the chromatograms in the part of the chromatogram where homo PS makes no contribution. So in this case, the value of x is $0.3/[(h/h') - 0.28]$ with $x_1 = 0$. More generally, for any x_1 this x gives the variation of the fraction of PS with the \bar{M}_n and is an interesting value to compare with the fractionation curves.

RESULTS AND DISCUSSION

The two reactants characterized by GPC have the following \bar{M}_n (in this domain of elution, the values obtained for the standards are close to the theoretical, so no correction is made):

$$\bar{M}_{n(\text{PVC})} = 35,000 \quad \bar{M}_{w(\text{PVC})} = 67,000 \quad (\bar{M}_{n(\text{PVC})} \text{ osmometry} = 33,000)$$

The values for the grafts are contained in Table I. They exhibit a polydispersity of 1.4. The agreement between predicted $\bar{M}_n = (\text{styrene})/(n\text{-BuLi})$ and the observed values is good, except for run number 32, where the $n\text{-BuLi}$ solution was aged and where the number of active initiating species was low, leading to higher \bar{M}_n .

The three main observations deriving from consideration of the chromatograms of the reaction products are: (a) the elution volume of the PVC after grafting is almost unchanged; (b) the amount of homo PS is large; (c) the PS grafts are uniformly fixed on the PVC chains.

a. The increase in molecular weight consequent to the grafting does not lead to a decrease of the elution volume. This would be the case for block copolymer, but here the second component is placed as branches, so the viscosity tends to decrease and the hydrodynamic volume is unchanged.

b. The part of the chromatogram, particularly the UV trace, at the higher elution volumes gives an idea of the unreacted PS. The PS contents of the mixture calculated by three methods are shown in Table II and are in good agreement. After decomposition of the PS chromatogram, the composition and the resulting \bar{l} compared to that deduced from the synthesis are in Table III. The ratio \bar{l}/\bar{l}' is very low at low amount of added PS but increases with this amount of PS. It does not seem that a saturation occurs rapidly, since the curve \bar{l}/\bar{l}' versus \bar{l}' does not exhibit an incurvation up to $\bar{l} = 6.2$ (Fig. 4). The five reactions have been made in five different runs, but the results may be plotted nicely on a simple curve. That means that they are reproducible and that grafting is

TABLE I
Synthesis of the Polystyrene Grafts^a

No.	Weight of styrene, g	$n\text{-BuLi}$, mole $\times 10^4$	\bar{M}_n theoretical	\bar{M}_n GPC uncorrected
2	2.1	4.0	5250	5900
4	4.5	8.8	5100	5800
6	6.15	10.5	5850	5450
8	8	16.0	5000	5150
32	20	37.0	5400	8500

^a In each case, 8 g PVC in 400 ml THF; $T = -60^\circ\text{C}$.

TABLE II
Weight-% of Polystyrene in the Mixtures

	Polystyrene, wt-%				
	No. 2	No. 4	No. 6	No. 8	No. 32
Synthesis	20.8	36	43.5	50	71.5
Static UV	20.5	35	43.5	52.5	76.5
GPC	22	32.5	45.5	50	80

TABLE III
Composition of Reaction Products. Expected \bar{l}' and Experimental \bar{l} Grafting Ratios

No.	Weight-% of			Effective \bar{l} grafting ratio	Theoretical \bar{l}' grafting ratio
	PVC	Homo PS	Graft PS		
2	78	19	3	0.2	1.47
4	67.5	20.2	12.3	1	3.2
6	54.5	29.5	16	1.7	4.65
8	50	29	21	2.8	6.4
32	23.5	32.5	37.5	6.2	9.7

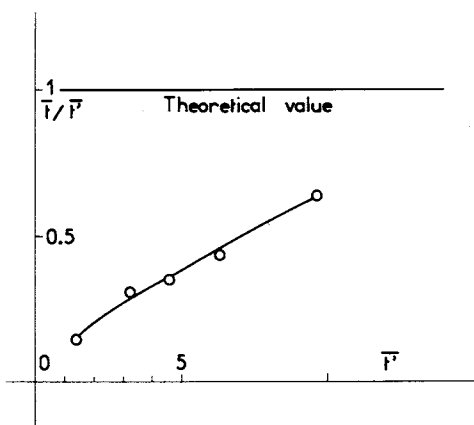


Fig. 4. Evolution of quantity \bar{l}/\bar{l}' ; average experimental to theoretical grafting ratios vs. theoretical ratio \bar{l}' .

operating randomly. Since the ratio \bar{l}/\bar{l}' increases with \bar{l}' , it may be supposed that secondary reactions and poisoning take place at a constant level, thus effective chiefly when the number of reactive chain ends is low. From Table III it may be seen that the amount of homo PS varies only slightly (19% to 32.5%) when the amount of living PS is changed of an order of magnitude.

c. After the decomposition of the chromatogram has been made, the respective contributions of PVC and g-PS are known (Fig. 2). The two deviations are in an almost constant ratio. This indicates a constant number of graft per Cl, independent of the chain length of the backbone. This fact is not surprising since only a very small number of Cl (1%) is concerned.

From the analyses of the fractions obtained from certain runs, it may be seen (Table IV) that the homo PS (Fig. 5) is never completely eliminated in the fractionation. (The UV detection is particularly sensitive to the PS.) It is

TABLE IV
Composition of the Fractions

Fraction no.	Weight-% of		
	PVC	homo PS	g-PS
Sample 2			
1	95.5	2	2.5
2	97.2	1.3	1.5
3	90.2		9.8
4	13		87
Sample 8			
1	50	20	30
2	50	20	30
3	50	20	30
4	27	62	11
5	12	83	5

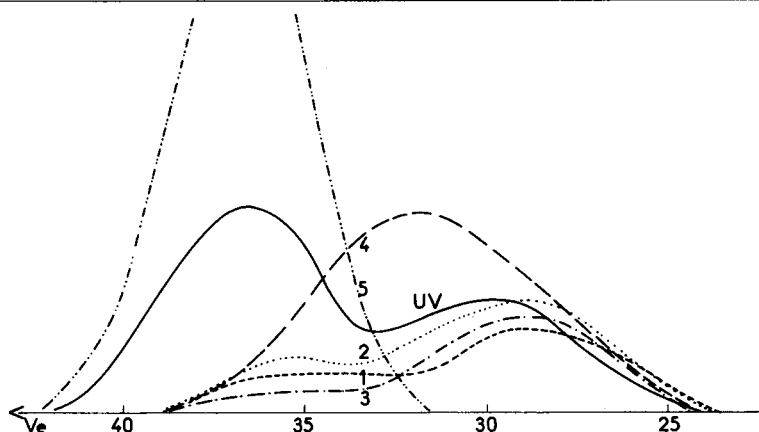


Fig. 5. UV chromatograms of product 8 and of its fractions.

surprising since the γ values of the PVC and PS are very different (Fig. 6). Only a few short chains are present in the PVC, the \bar{M}_n of PVC and PS are very different, and only some branches of PS are fixed on PVC. Samples 8-1,2,3 and 2-1,2,3 must be free of homo PS; but the respective difference with 8-4,5 and 2-4 is only a large change in the PS content (30% to 70% and 10% to 80%). That means that the behavior of the mixtures is similar to that of PS.

Table V gives a comparison between the PS content in the fractions calculated by static UV and GPC. The latter method leads to higher results for sample 8 and lower results for sample 2. In the last column are the values calculated from the summation of the fractions

$$\Sigma \% = \frac{\Sigma m_i (\% PS)_i}{\Sigma m_i}$$

The GPC results are those obtained on the whole sample.

In the same way, Figure 3 shows a correct agreement between the chromatogram of the figure and those calculated from the chromatograms of the fractions and their weight. In fact, several errors are added (inaccuracy of the weights of injected samples), explaining some difference in the two curves, that do not

TABLE V
Analysis of the Fractions of Runs 2 and 8*

Fraction	No. 1	No. 2	No. 3	No. 4	No. 5	Σ
Copolymer 2						
γ (THF-hexane)	0.54	0.593	0.74	1		
Weight of fraction	3.342	1.287	1.120	1.193		6.942
Weight-% of styrene						
UV	7	6.6	11.7	82.5		20.5
GPC	4.5	2.8	9.8	87		22
Copolymer 8						
γ (THF-hexane)	0.639	0.657	0.673	0.856	1	
Weight of fraction	0.835	2.075	1.070	1.190	1.645	6.815
Weight-% of styrene						
UV	28	27	31	58	69	42.5
GPC	35	30	34	73	88	50

* Initial weight 7 g in 700 ml THF.

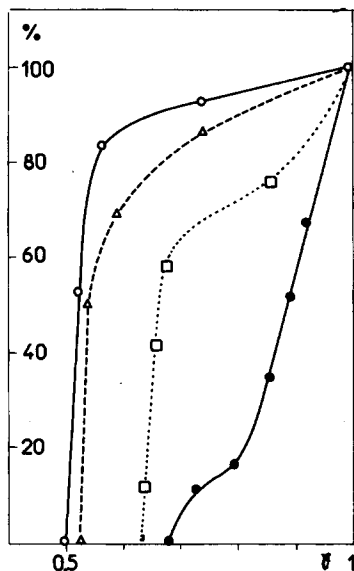


Fig. 6. Fractionation curves for PVC (O), PS (●), and products 2 (Δ) and 8 (□): wt-% of polymer according to γ (for THF-hexane).

occur in the relative measurements mentioned in method (a). Turning back to the whole sample, the calculation of the molecular weight shows that the increase is important only for sample 32. An osmometric measurement was unable to see it since, as in all cases, the homo PS affects considerably the results, so that the \bar{M}_n of the mixture is lower than that of the initial PVC.

This fact and the other features presented at the beginning of the "results" prove the interest and accuracy of the GPC method. This technique has been extended to the study of similar reactions with interpretation of the results.¹⁰

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Received December 2, 1974