

Bromination of Polystyrene with N-Bromosuccinimide, Debromination of the Brominated Polystyrene and Grafting of Vinyl Acetate on the Backbone of Debrominated Polystyrene

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A polymer, which has some double bonds in the polystyrene linear chain, was prepared. The vinyl acetate monomer was polymerized using benzoylperoxide as initiator in the presence of the unsaturated polystyrene-derivative. The polymer obtained was soluble both in benzene and methanol. The authors have analyzed this polymer and confirmed that this is the graft-copolymer, which has the polystyrene-stem and polyvinyl-acetate-branches.

Polystyrene was brominated with N-bromosuccinimide, using benzoyl peroxide as a catalyzer. It is obvious that the bromination occurs by this process radically at the α -carbon to the benzene nucleus. The brominated polystyrene was the dehydrobrominated by treating with sodium butylalcoholate solution. By this treatment some double bonds should be produced in the linear chain of the polystyrene. Further the vinyl acetate monomer was polymerized in the presence of the above debrominated polystyrene polymer. By examining the polymer thus obtained, the authors have proved that the graft-copolymer of vinyl acetate on the backbone of debrominated polystyrene was formed.

EXPERIMENTAL

(1) Materials

N-Br-succinimide (NBS) was prepared after the method of K. Ziegler.¹⁾ The commercial polystyrene was used; the polymerization-degree determined viscometrically was 3200.

(2) Bromination of Polystyrene with NBS

The bromination of polystyrene with NBS was performed after the usual procedure of Wohl-Ziegler's reaction.²⁾ For example (Table 1, exp. No. 6), 22.5 g. polystyrene was dissolved in 300 cc. carbon tetrachloride, 44 g. NBS and 11.0 g. benzoyl peroxide, was added and then the mixture was refluxed under stirring. The reaction solution became brownish under foaming. After 220 minutes heating, the succinimide was filtered off, the filtrate was concentrated in vacuo and poured

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into methanol. The brominated polymer precipitated as powder. This was separated by filtration and dissolved again in benzene. The benzene solution was centrifuged in order to remove some insoluble matter and poured again in methanol. This purification process was repeated three times. The purified brominated polystyrene was dried in vacuo (4-5 mm. Hg) at room temperature and its Br-content was analyzed by Carius-method. The results obtained under various conditions, are given in Table 1.

Table 1.

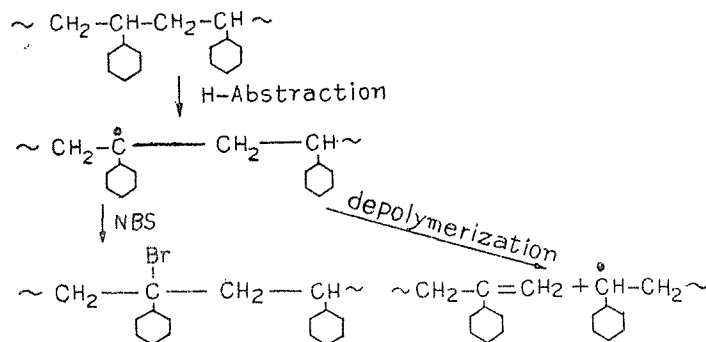
Ext. No.	Conditions of bromination						Br-content	
	Poly-styrene (g.)	NBS (g.)	Mole-ratio ^{a)} PSt/NBS	BPO (g.)	CCl ₄ (cc)	Reaction time ^{c)} (hours)	Wt. %	unit % ^{b)}
1	6.25	11.76	1.1	0.240	36	6 $\frac{5}{8}$	3.10	4.19
2	6.29	11.80	1.1	0.060	40 ^{c)}	1 $\frac{1}{2}$	4.36	5.94
3	10.40	19.80	1.1	2.320	100	1	28.7	52.1
4	22.50	44.00	1.1	5.200	300	2 $\frac{1}{2}$	18.7	29.8
5	22.50	44.00	1.1	11.000	300	3 $\frac{3}{8}$	32.0	60.7
6	10.40	19.80	1.1	2.320	150	5	18.6	29.7
7	10.40	19.80	1.1	1.660	150	5	15.9	24.6
8	20.80	35.60	1.0	9.680	280	1	21.1	34.8

^{a)} Moles of styrene-unit in polystyrene were taken for the calculation.

^{b)} Number of brominated styrene-units per 100 styrene-units in the polymer.

^{c)} Benzene was used instead of CCl₄.

The viscosities of the brominated polymers have dropped to some degree compared with the original polymer. As the bromination by this method is a radical nature,⁹⁾ it can be assumed that depolymerization occurred simultaneously as shown in the following reaction scheme :



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The viscosities of the original polystyrene, brominated polystyrene (No. 5..... sample PB-1) and ditto (No. 9..... sample PB-3) are given in Tables 2, 3 and 4 in Figs. 1 and 2. The molecular weights of the brominated polystyrenes were calculated from the viscosity by the same equation as the polystyrene itself.

$$[\eta] = 1.7 \times 10^{-4} \times [M]^{0.72}$$

Table 2.
Viscosity of the original polystyrene

C (g/100 cc)	η (sec.)	η_{sp}/C
1.483	352.8	2.72
0.742	196.9	2.44
0.376	123.9	2.04
0.190	94.0	1.81
0.100	82.1	1.73
$M \approx 332,900$; $\bar{P} \approx 3,200$		

Table 3.
Viscosity of PB-1.

C (g/100 cc)	η (sec.)	η_{sp}/C
2.710	125.9	0.295
1.355	94.5	0.259
0.904	86.3	0.258
0.602	80.8	0.257
$M \approx 25,780$; $\bar{P} \approx 250$		

Table 4.
Viscosity of PB-3.

C (g/100 cc)	η (sec.)	η_{sp}/C
2.899	105.2	0.174
1.938	92.2	0.165
1.292	84.5	0.159
0.863	79.2	0.154
$M = 11,880$; $\bar{P} \approx 114$		

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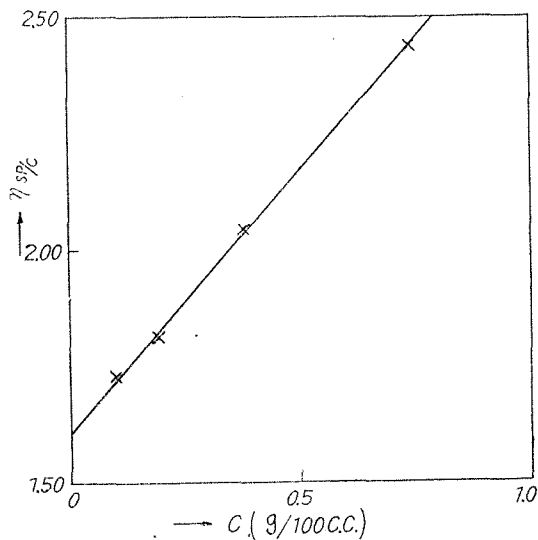
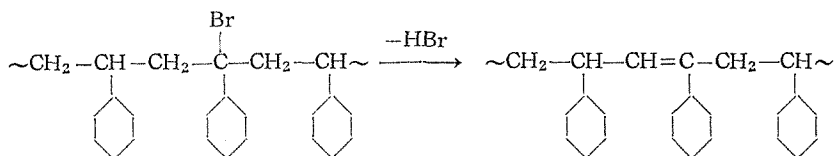


Fig. 1. Viscosity of the original polystyrene.

3. Debromination from the Brominated Polystyrene -- Formation of Double Bond

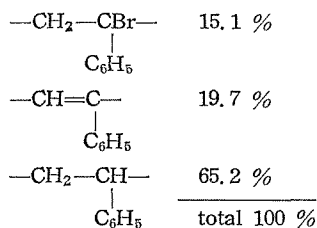


The brominated polystyrene was dissolved in benzene and this solution was treated with sodium-butylalcoholate. For example, 10.0038 g. of PB-1 was dissolved in 350 g. benzene, mixed with a sodium-butylalcoholate solution, prepared from 7g. sodium and 100 cc. *n*-butanol, and then refluxed for 10 hours. After cooling, the reaction mixture was poured into methanol, which contained a small quantity of water and the separated polymer was filtered. This polymer was dissolved again in benzene and precipitated with methanol. This purification process was repeated three times. The yield of dried product (sample PC-1) was 5.95 g. and its Br-content was found as 8.37 %.

About this debrominated sample PC-1 it can be calculated that this sample has the following proportion of three parts of different structures.

$-\text{CH}_2-\overset{\text{C}_6\text{H}_5}{\text{C}}\text{Br}-$	11.8 %
$-\text{CH}=\overset{\text{C}_6\text{H}_5}{\text{C}}-$	49.1 %
$-\text{CH}_2-\underset{\text{C}_6\text{H}_5}{\text{CH}}-$	39.1 %
	<hr/> total 100 %

Similarly the PB-3 (10 g.) was submitted to debromination. The yield of the debrominated product (PC-4) was 7.52 g. and its Br-content was found as 9.24 %. About this PC-4 the following values were also calculated.



The brominated polystyrene, 10 g. (PB-1) was dissolved in 200 g. benzene and debrominated by refluxing for 9 hours with a sodium-butylate solution, prepared from 4.7 g. sodium and 800 cc. *n*-butanol. The debrominated product consists of two parts, the one is soluble in benzene (PC-2) and the other is insoluble in benzene (PC-3). The benzene-insoluble parts are considered to have been produced by the secondary polymerization of double bond formed by debromination. The soluble part was purified by repeated precipitation. Both portions were analyzed and the proportion of the three parts of different structures was calculated as given below :

	PC-2 (Benzene-soluble)	PC-3 (Benzene-insoluble)
Yield	1.86 g	6.39 g
Br-content	15.30 %	14.60 %
$\text{---CH}_2\text{---CBr---}$ $\quad \quad $ $\quad \quad \text{C}_6\text{H}_5$	23.4 %	21.1 %
---CH=C--- $\quad \quad $ $\quad \quad \text{C}_6\text{H}_5$	37.3 %	38.6 %
$\text{---CH}_2\text{---CH---}$ $\quad \quad $ $\quad \quad \text{C}_6\text{H}_5$	39.3 %	39.3 %

The viscosities of the debrominated polymers were measured and the results are given in Table 5, 6 and in Fig. 2. The viscosities are greater than those of

Table 5.
Viscosity of PC-2

C (g./100cc.)	η (sec.)	η_{sp}/C
3.044	130.3	0.282
1.522	93.3	0.218
1.020	84.3	0.200
0.684	79.0	0.188

$M \approx 13,850$,

$P \approx 130$

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the corresponding brominated samples. This phenomena are clearly due to the secondary polymerization of the double bond, formed by debromination.

Table 6.
Viscosity of PC-4

C(g./100cc.)	η (sec.)	η_{sp}/C
1.902	157.1	0.648
0.954	101.0	0.458
0.544	84.5	0.372
0.365	79.2	0.344

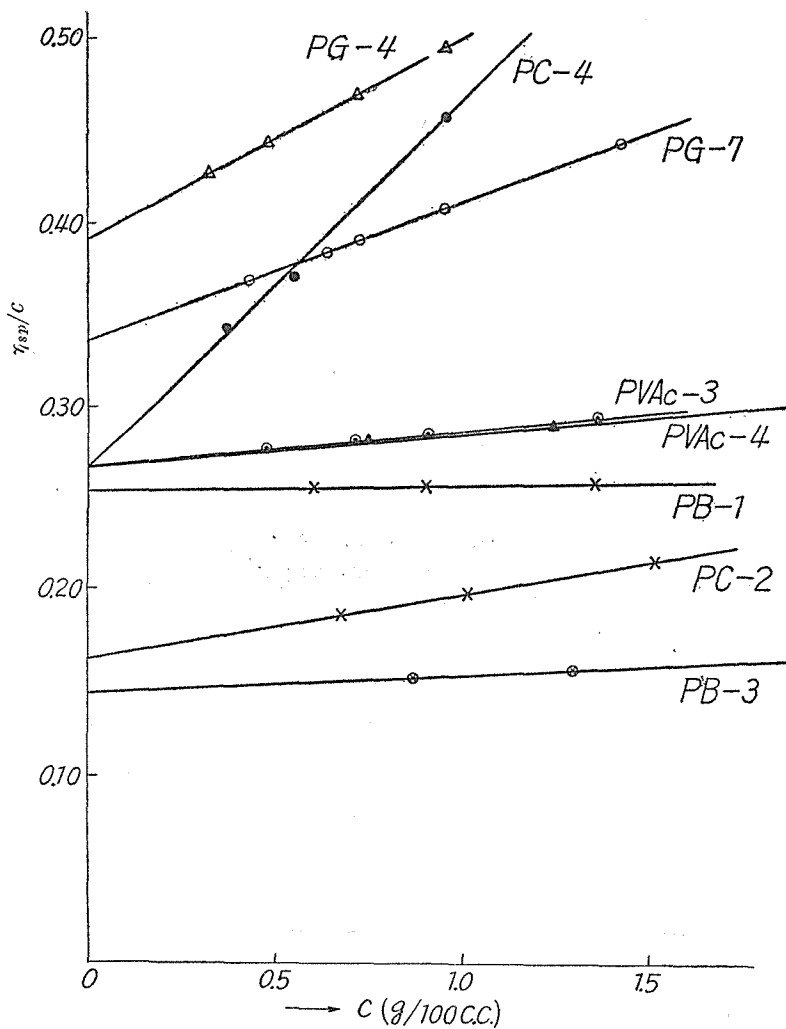
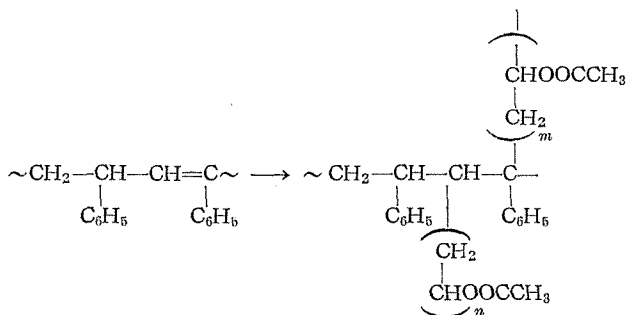


Fig. 2

4. Preparation of Graft-copolymer

Using the above obtained debrominated polymer as the backbone, the vinyl acetate was grafted. The structure of the obtained graft-copolymer could be written as follows :



Experiment 1, (in flask).

A sample of 0.980 g. of the debrominated polymer PC-1 (content of unsaturation=49.1%) was dissolved in 10 cc. benzene, 10 g. vinyl acetate and 0.30 g. benzoyl peroxide were added and the mixed solution was refluxed under stirring for 13 hours. The product separated into two portions, the one was soluble in benzene (4.79 g.....PG-1) and the other insoluble (0.299 g.....PG-13). The former (PG-1) is soluble not only in benzene, but also in methanol. Therefore it may be suggested that this PG-1 is a mixture of the aimed graft-copolymer and the polyvinylacetate. In order to know the content of straight polyvinylacetate in PG-1, the saponification equivalent was determined. 0.15 g. of PG-1 was dissolved in 10 cc. methanol, 10 cc. of 0.1 N methanolic caustic soda solution was added and after definite period of heating the solution was acidified with 20 cc. of 0.1 N H₂SO₄ and the excess H₂SO₄ was backtitrated with 0.1 N NaOH solution (f=0.805). The results thus obtained are summarized in Table 7.

Table 7.

Temp.	Hours	Number of ml. of NaOH solution consumed per 0.1g. sample
Room temp.	40	1.06
70°	1	4.24
80°	2.5	7.32
80°	4.0	11.62
80°	6½	11.59

From the above results it is concluded that graft-copolymer PG-1 is more

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difficult to be hydrolyzed than the straight polyvinylacetate and for the complete saponification 4-hr. heating at 80°C is necessary. From the above obtained saponification value the content of vinyl acetate in 4.79 g. PG-1 is calculated as 3.85 g. The difference, 4.79 g.-3.85 g, is the portion of polystyrene-backbone. The benzene-insoluble portion (PG-13) resulted from the secondary polymerization of the double bond and, when assumed that the vinyl acetate is contained also in this benzene-insoluble part at the same proportion as in the benzene-soluble part (PG-1), the amount of the total polystyrene-backbone is calculated as 0.99 g. This value coincides very well with the quantity of PC-1, which was used at first for this experiment.

The Br-content of PG-1 was also measured and found as 0.0101 g. AgBr from 0.2533 g. sample. From this value the polystyrene-backbone in PG-1 (4.79 g.) was calculated as 0.940 g. and this value coincide well with the value which was calculated above from saponification value.

Experiment 2, (in sealed tube)

Contrary to the above mentioned results in flask, the product, graft-copolymerized in sealed tube, was all soluble in benzene and methanol. At the same time the vinyl acetate was polymerized in the presence of polystyrene or brominated polystyrene. In these two cases the polystyrene or brominated polystyrene were recovered completely from the polymerized product as in methanol insoluble portion. These results are same as those of Smets⁴⁾. The precise experiment conditions are as follows :

Sealed tube No. 1.

PC-2 1.000 g., benzene 10 cc., vinyl acetate 10 cc., BPO 0.2 g.

Sealed tube No. 2.

PB-1 (brominated polystyrene) 1.000 g., benzene 10 cc.,
vinyl acetate 10 cc., BPO 0.2 g.

Sealed tube No. 3.

Polystyrene 1.000 g., benzene 10 cc., vinyl acetate 10 cc., BPO 0.2 g.

The sealed tubes 2 and 3 were heated at $75 \pm 0.1^\circ\text{C}$. for 24 hours and the sealed tube 1 was heated at $75 \pm 0.1^\circ$ for 24 hours, at 80° for 24 hours and further at 85° for 12 hours.

The polymer of sealed tube 1 was soluble in benzene and methanol. From methanolic solution the polymer was precipitated by adding water. The yield of the purified and dried polymer was 3.9923 g. (PG-2).

About this PG-2 the saponification equivalent was measured as before and the content of the polyvinylacetate was calculated as 3.02 g. The difference, 3.99-3.02 g. = 0.97 g, is the quantity of the polystyrene-backbone. This value coincides well with the amount of PC-2, which was used at first.

As the PG-2 is a mixture of the aimed graft-polymer and a straight polyvinyl-

acetate, this was treated as follows, in order to separate the each component. A sample of 2.5026 g. of PG-2 was dissolved in 150 cc. methanol, 1.20 g. NaOH was added and refluxed for 4 hours. The saponified, precipitate polymer was filtered through glass-filter, washed with methanol and dried. The yield was 1.5274 g. This saponified polymer was extracted continuously with boiling water for 3 hours in order to dissolve out the straight polyvinylalcohol. The water-insoluble portion was 0.8904 g. (PG-3) and the water soluble portion 0.5825 g. (PVA-1).

PG-3 (0.8456 g.) was reacetylated by refluxing together with a mixture of 8 cc. pyridine and 4 cc. acetic anhydride on an oil bath at $130 \pm 5^\circ\text{C}$ for 4.5 hours. The PG-3 was at first insoluble, but as the reaction proceeded it went into solution completely. The reaction solution was poured into water and the precipitated polymer was filtered, washed with water and dried. The yield of thus reacetylated polymer (PG-4) was 1.1131 g.

The saponification value of this PG-4 was then measured and found that 8.64 cc. 0.1 *N* NaOH ($f=0.805$) was consumed for 0.1200 g. PG-4.

From this value the amount of the grafted vinyl acetate was calculated as 0.0597 g. From the difference, $0.1200 - 0.0597$, the amount of the polystyrene-backbone in the original PG-2 was calculated as 0.945 g. This value coincides within experimental error with the quantity of debrominated polystyrene, which was used at first for this experiment (1.000 g.). From these results it can be concluded that all of the debrominated polystyrene had participated in the formation of graft-copolymer and this graft-copolymer consists of 0.945 g. polystyrene-backbone and 0.933 g. polyvinylacetate-side chain. The authors have examined further the ultraviolet absorption spectrum of the water soluble PVA-1 and could not recognize any band, corresponding to polystyrene.

Table 8.
Viscosity of the reacetylated graft-copolymer (PG-4)

C(g./100 cc)	η (sec)	η_{sp}/C
3.426	281.4	0.868
1.713	143.6	0.608
0.951	103.5	0.497
0.712	93.8	0.471
0.474	85.1	0.445
0.316	79.8	0.428

The polymer from the sealed tube-2 was poured into methanol and the precipitated polymer was washed with methanol and dried. The yield was 0.96 g. This was identified to be the same as the original brominated polystyrene.

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Methanol-soluble polymer was not found at all.

The polymer from the sealed tube-3 was also poured into methanol and the precipitated polymer was separated as above. The yield was 0.997 g. From the methanol solution 0.370 g. polymer was recovered. The former is identical with the original polystyrene and the latter, methanol-soluble polymer, is the straight polyvinylacetate. The authors have also proved that the polyvinylacetate formed in this sealed tube-3 is of the same polymerization degree as the polyvinylacetate (PVA-1) in sealed tube-1.

REFERENCES

- (1) K. Ziegler, *Ann. d. Chem.*, **551**, 80 (1942).
- (2) C. Djerassi, *Chem. Revs.*, **43**, 271 (1948).
- (3) P. Goldfinger, *Nature*, **168**, 30 (1951).
- (4) G. Smets, *J. Polymer Sci.*, **8**, 289 (1952).