

Anionic Graft Copolymers. II. Extension of Techniques of Preparation and Characterization

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Synopsis

Graft copolymers with poly(vinyl chloride) backbones and controlled amounts of polystyrene, poly(1,2-butadiene), or poly(1,2-butadiene-styrene) are prepared by carbanionic deactivation. Synthesis is by two methods: a classical step-by-step anionic polymerization technique and a new one-apparatus technique. The reaction products are characterized by osmometry, selective extraction, and gel permeation chromatography to test the consistency of the three methods. A few words are said about the yields of grafting compared with temperature, size, and nature of carbanions.

INTRODUCTION

In a previous paper, we proposed a GPC technique for the analysis of graft copolymers of poly(vinyl chloride) (PVC) and polystyrene (PS).¹ Here, the grafting is extended to different polymers on the PVC backbone, and some change in the process is proposed to obtain better reproducibility. Several characterization techniques are used.

As is known, the graft copolymers prepared by carbanionic deactivation are of great interest as they are well defined² and can be used to study the properties of solid polymers as block copolymers.^{3,4} The studies of morphologic and mechanical properties of such copolymers presuppose primarily a good knowledge of their structure and composition.

In order to have well-defined copolymers, we propose an apparatus which allows us to obtain the graft copolymers without sealing together any parts, and which gives us samples easiest to get and much more reproducible. Contamination is avoided and the same polymer is used for grafting at different extent along a given backbone.

These samples are studied by several techniques (GPC, selective extraction, osmometry). The validity of these techniques is compared to let us use one or another when it will be the only one available. A critical study of the results shows a good consistency of the characterization methods.

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EXPERIMENTAL AND RESULTS

Preparation of Polymers

a. The step-by-step method of anionic grafting is of the type generally used in our laboratory:⁵ the reagents and solvent are purified, and kept and transferred under high vacuum through break seal.

b. The process is basically the same, but a special apparatus (Fig. 1) is used which allows us to make a one-step copolymerization as all the reagents are kept around the reactors which are filled by vacuum distillation or through Rotaflo stopcocks. The reactors are set to the correct temperature by cold methanol circulation (Ultra Kryostat Lauda K 90) or warm water circulation. The temperature of the R_1 and R_2 reactors are regulated ($\pm 0.1^\circ\text{C}$) and known ($\pm 0.5^\circ\text{C}$).

The solvent is poured into a first reservoir B_1 , where a drying agent is added (a) (sodium, CaH_2 , Na-K alloy or styryl anions) and is later distilled under vacuum in a flat-bottom flask B_2 , to which we can add (b) a colored reagent (e.g., polystyryl carbanions) and check the absence of moisture in the solvent which is kept at -60°C for never more than a fortnight.

In a typical experiment, for the preparation of PVC-g-PS (series PS I), we pour (c) 8 g commercial PVC (Rhône-Progil, mass process, $\bar{M}_n = 33,000$) which is dried under high vacuum (10^{-5} mm Hg). Solvent, 400 ml, is added by distillation (d) and the solution is stirred for 24 hr while 400 ml THF is distilled in the reactor R_1 (-60°C) (e). A 0.133*N* solution, 12 ml, of *n*-butyllithium in hexane is added (f) (1.6×10^{-3} mole). Styrene kept at low temperature is warmed and added immediately (g) by distillation (19 g; 0.183 mole) to avoid reaction between *n*-BuLi and THF⁶ which is slow at this temperature. The reactor is left to allow complete polymerization at which point the molecular weight is 12,000, as expected.⁶ Then, 50 ml of this living polymer solution (2×10^{-4} chain of PS⁻) is poured into the R_2 reactor (i). This polymer is able to react

TABLE I
Grafting of PS on PVC at $+30^\circ\text{C}$ in THF

No.	Weight of recovered polymer, g		Styrene, %		l^a
	Theoretical	Experimental	Theoretical	Experimental (UV)	
PSI 1	1.81	1.75	22.9	23.5	0.56
PSI 2	2.06	1.99	44.2	45.2	1.51
PSI 3	2.40	2.06	58.3	57.8	2.51
PSI 4	2.57	2.10	66.0	65.0	3.40
PSI 5	3.78	3.09	73.0	74.5	5.36
PSI 6	5.50	4.23	78.8	82.0	8.35
PSI 7	8.35	7.97	83.5	83.0	8.95
PSI 8 ^b	0.50	0.53	100	100	..
TOTAL	26.97	23.72 (88%)			

^a l^a means the theoretical number of PS chains per PVC backbone.

^b PSI 8 is the living polystyrene in R_1 .

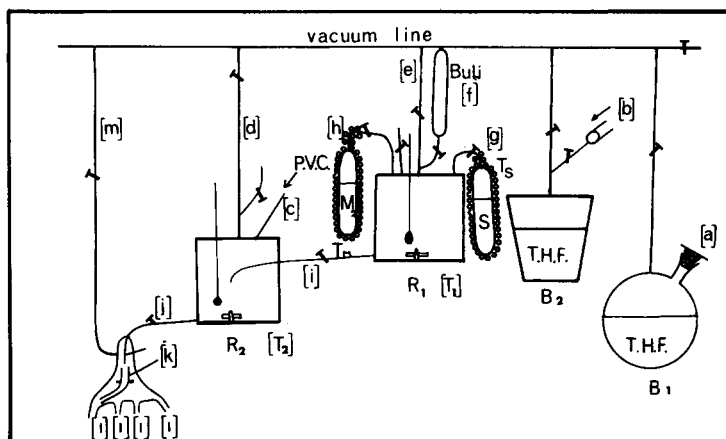
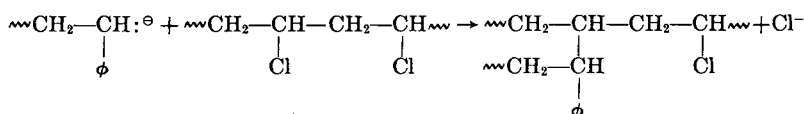


Fig. 1. The new copolymerization apparatus.

with the 2.4×10^{-4} chain of PVC and leads to an average number \bar{l} of grafts of 0.83 for one PVC chain:



Of the solution from R_2 (j), 80 ml is taken off and poured in a small flask (1) connected to the collector, monitored by an external magnet. At this time, 350 ml (1.4×10^{-3} mole of PS^-) is in R_1 and 320 ml (1.92×10^{-4} mole of PVC already 0.83 grafted) is in R_2 . As the process is repeated, higher theoretical grafting yields are obtained (Table I). The polymers are precipitated in methanol, dried under vacuum, and weighed; the amount of styrene is calculated from the UV absorbance at 260 m μ .

The other syntheses are reported in Table II. The PVC graft polybutadiene is referenced PB. Different molecular weights of polybutadiene are used. For block polystyrene-polybutadiene grafts, the molar fraction of styrene is 0.95. The butadiene is added to the living polystyryl. The reference is PS III.

Selective Extraction

In some cases, one component of the graft copolymer-homopolymers mixture can be selectively extracted. The unreacted polybutadiene chains can be solubilized in cyclohexane; 2 g of the mixture is left for 12 hr in 200 ml cyclohexane. The light suspension of insoluble PVC and PVC-g-PB graft copolymer is centrifuged for 1 hr at 2500 rpm and the solution is then separated (homopolybutadiene). The two parts are weighed, and chlorine contents⁷ are measured by potentiometric titration after mineralization (Table III). A good separation is obtained as confirmed by the GPC chromatograms (Fig. 2).

Osmometry

In this range of molecular weight, osmometry may be used with confidence. A Melab osmometer with ortho-dichlorobenzene at $+60^\circ\text{C}$ is used. Since the molecular weights of grafts and backbones (\bar{M}_G and \bar{M}_{PVC}) as well as the weight

TABLE II
 Synthesis of Graft Copolymers with PVC Backbones

No.	Nature of grafts	T, °C	$(\bar{M}_n)_G^a$		<i>l'</i>	Method
			Theoretical	GPC		
PB 25	polybutadienyl	-60°	—	25,000	0.48	conventional step-by-step technique
PB 50	polybutadienyl	-60°	9,000	13,000	2.16	
PB 70	polybutadienyl	-60°	—	22,000	3.11	
PB 701	polybutadienyl	-60°	11,800	14,000	4.38	
PB 75	polybutadienyl	-60°	8,500	10,400	6.15	
PSIII 1	poly(styrene-co-butadienyl)	+30°	14,000	15,000	0.89	special one-apparatus technique
PSIII 2	poly(styrene-co-butadienyl)	+30°	14,000	15,000	2.42	
PSIII 3	poly(styrene-co-butadienyl)	+30°	14,000	15,000	3.44	
PSIII 4	poly(styrene-co-butadienyl)	+30°	14,000	15,000	5.39	
PSIII 5	poly(styrene-co-butadienyl)	+30°	14,000	15,000	7.36	
PSIII 6	poly(styrene-co-butadienyl)	+30°	14,000	15,000	16.90	
PSIII 7	poly(styrene-co-butadienyl)	+30°	14,000	15,000	46.60	

^a Molecular weight of the grafts.

 TABLE III
 Selective Extraction of Homopolybutadiene

No.	Analysis of mixture, wt-%		Weight-% insoluble	PVC contained in the insoluble, %		<i>l</i>
	PVC	PB		Calculated	Experimental	
PB 25	73.3	26.7	81	1.00	0.91	0.13
PB 50	54.0	46.0	70	0.772	0.773	0.74
PB 70	32.5	67.5	53	0.613	0.615	0.94
PB 701	35.0	65.0	58	0.608	0.610	1.51
PB 75	39.0	61.0	65	0.500	0.507	3.08

of PVC (*P*) and of polybutadiene (*G*) are known, we can calculate the apparent osmometric molecular weight \bar{M} :

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{n_1 \bar{M}_G + n_2 (\bar{M}_{PVC} + l \bar{M}_G)}{n_1 + n_2}$$

where n_1 = number of chains of unreacted polymer to be grafted, n_2 = number of chains of PVC backbones, X = total number of chains of grafts, and l = experimental grafting yield. Then,

$$\bar{M}_n = \frac{X \bar{M}_G + n_2 \bar{M}_{PVC}}{n_2 + X - l n_2}$$

$$l = \frac{X(\bar{M}_n - \bar{M}_G) + n_2(\bar{M}_n - \bar{M}_{PVC})}{n_2 \bar{M}_n}$$

TABLE IV
Experimental Grafting Yield Derived from Osmometric Measurements

No.	\bar{M}_G	\bar{M}_n	\bar{v}'	P	\bar{i}
PB 25	25,000	34,000	0.48	0.73	0.15
PB 50	13,000	25,000	2.16	0.54	0.72
PB 70	22,000	37,000	3.11	0.325	1.35
PB 701	14,000	23,300	4.38	0.35	1.33
PB 75	10,400	20,000	6.15	0.34	2.30

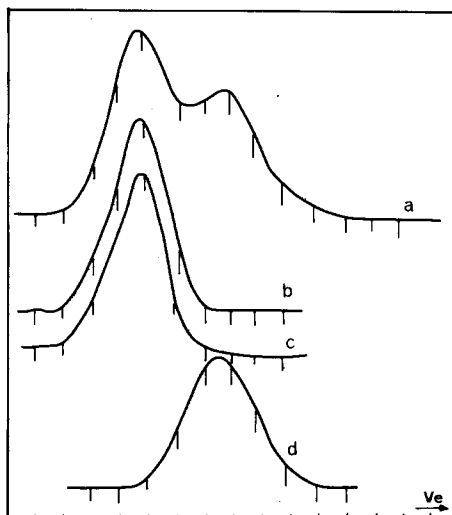


Fig. 2. GPC control of selective extraction: (a) mixture before extraction; (b) PVC-PB insoluble in C_6H_{12} ; (c) initial PVC; (d) homo PB soluble in C_6H_{12} .

By using the weight contents G and P , one gets

$$\bar{i} = 1 + G\bar{M}_{PVC}/P\bar{M}_G - \bar{M}_{PVC}/P\bar{M}_n.$$

Since

$$\bar{v}' = G\bar{M}_{PVC}/P\bar{M}_G$$

$$\bar{i} = 1 + \bar{v}' - \bar{M}_{PVC}/P\bar{M}_n \quad (\text{Table IV}).$$

Gel Permeation Chromatography (GPC)

The application of the gel permeation chromatography technique with dual detection has been described in a previous paper.¹ The analysis of a mixture of polymer and copolymer is very easy when only one component (i.e., polystyrene) shows an UV absorbance, but the method may be extended to the general case with only one refractometric detection.

The chromatograms generally show two overlapping peaks. They can be decomposed with a curve analyzer. The large elution volume peak (area A) is due to ungrafted living polymer, and the other (area A') is characteristic of the graft copolymer (with an average grafting yield \bar{i}). If the refractometric responses (area per gram) of the backbone and the grafts are C and G , the analysis

TABLE V
 GPC Analysis of a Mixture of Homopolybutadiene and Graft Copolymer Through a
 Single Refractometric Detection Technique

No.	A, mm ²	A'	π	c/g	cC/gG	y'	l'	l
PB 25	3865	7145	0.347	2.745	2.075	1.07	0.48	—
PB 50	3225	8395	0.271	1.17	0.882	0.51	2.16	1.06
PB 70	4955	6410	0.430	0.481	0.363	0.59	3.11	1.28
PB 701	6854	8242	0.444	0.538	0.406	0.62	4.38	1.66
PB 75	5386	5745	0.467	0.639	0.482	0.69	8.15	1.91

gives the weight c and g of each. We know that the average experimental grafting yield l compared with the theoretical one, l' , will be

$$l = y'' l'$$

for a given experiment. Hence, y'' is the ratio of reacted grafts to the total amount of grafts:

$$A = Gg(1 - y'')$$

$$A' = Ggy'' + Cc$$

which leads to

$$y'' = A'Gg - Cc/Gg(A + A').$$

If the relative area π of the A' peak is used,

$$\pi = A'/(A + A')$$

we get

$$y'' = 1 - \pi - \pi Cc/Gg \quad (\text{Table V}).$$

The C/G value is obtained by an injection of an equal amount of homopolymers and is 0.755.

The PS III series, which is made of block copolymer grafts of styrene and butadiene, can be analyzed also by a dual detector system¹ and the results of the different analyses are compared.

DISCUSSION

Accuracy of the Analyses

To test the accuracy of the methods of analysis, we looked into the results of the PB and the PSI series which have been analyzed several times (Table VI). Previously, we found that poisoning and secondary reactions took place at a constant level, reducing the grafting efficiency when a low amount of living chains was allowed to react with the PVC. By refining the technique, these reactions have been lowered, so that the experimental grafting yield l may be studied versus the theoretical one, l' . A pseudolinear correlation appeared, and a least-squares fitting including the point (0,0) was used. If we suppose that the grafting reaction is linear versus the number of the added grafts, this requires that we have neither steric hindrance nor autoacceleration of the grafting process along the chain, and the equation is

$$y = \bar{y} + m(x - \bar{x}).$$

TABLE VI
Analyses of Grafting Ratios Through Different Technique for Polybutadiene and Polystyrene Grafts

No.	\bar{v}'	\bar{i}			
		Extraction	Osmometry	Dual GPC	Single GPC
PB 25	0.48	0.13	0.15		0
PB 50	2.16	0.74	0.72		1.06
PB 70	3.11	0.94	1.35		1.28
PB 701	4.38	1.51	1.33		1.66
PB 75	6.15	3.08	2.30		1.91
PSI 1	0.56			0.27	—
PSI 2	1.51			0.75	0.75
PSI 3	2.51			1.10	1.20
PSI 4	3.40			1.68	1.50
PSI 5	5.36			2.58	2.60
PSI 6	8.35			4.05	3.80
PSI 7	8.95			5.10	—

TABLE VII
Least-Squares Fittings of the Grafting Yield \bar{i} vs. \bar{v}'

No.	Carbanion	T , °C	Method	Slope	σ	Probable error $t\sigma$ at 90%
PB	butadienyl	-60	extraction	0.47	0.130	0.25
	butadienyl	-60	osmosis	0.36	0.040	0.09
	butadienyl	-60	GPC single	0.34	0.090	0.20
	butadienyl	-60	all methods	0.39	0.031	0.05
PS I	styryl	+30	GPC single	0.47	0.060	0.11
		+30	GPC dual	0.53	0.036	0.07
		+30	all methods	0.51	0.024	0.04
PSIII	butadienyl	+30	GPC dual	0.39	0.030	0.06

The fitted curve passes at the point $\bar{x} = \bar{v}'$; $\bar{y} = \bar{i}$, and its slope is m . For each case, we can calculate the equation of the regression line, and we can estimate the dispersion with the second moment about μ^2 (variance), which is the square of the standard deviation σ , and compare the methods of analysis and the yields of grafting (Table VII).

It can be seen that the different methods of analysis give comparable standard deviations σ , and one or another method may be used when necessary. Yet, the extraction method seems to be less accurate. We also checked the accuracy of the GPC single-detector analysis ($\sigma = 0.060$), which, however, is less accurate than the dual detector ($\sigma = 0.036$).

Grafting Reaction

The variation in efficiency of grafting with carbanion concentration and temperature (Figs. 3 and 4) may be compared, and no significant influence of temperature on the grafting of polybutadiene on PVC is seen:

$$\text{At } -60^\circ\text{C } m_B = 0.39 \pm 0.05$$

$$\text{At } +30^\circ\text{C } m_B = 0.39 \pm 0.06$$

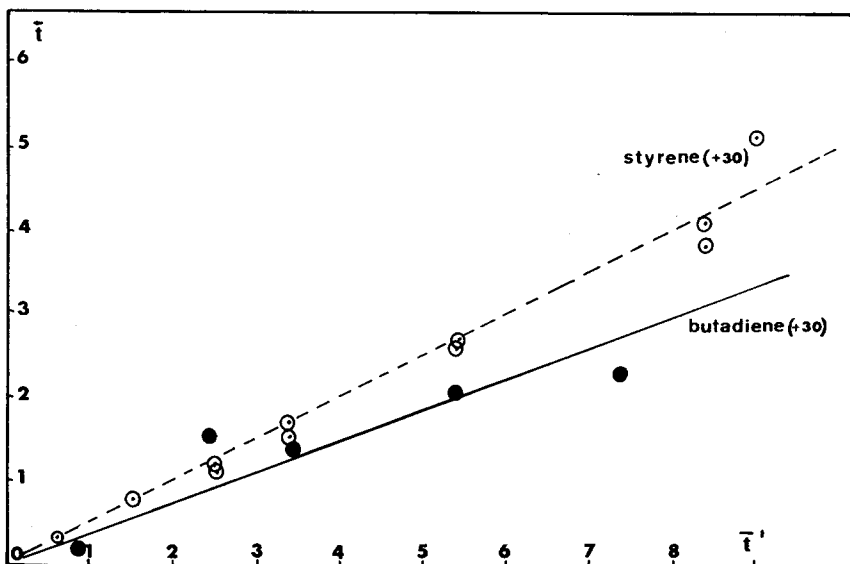


Fig. 3. Styrene (○) and butadiene (●) grafting at +30°C.

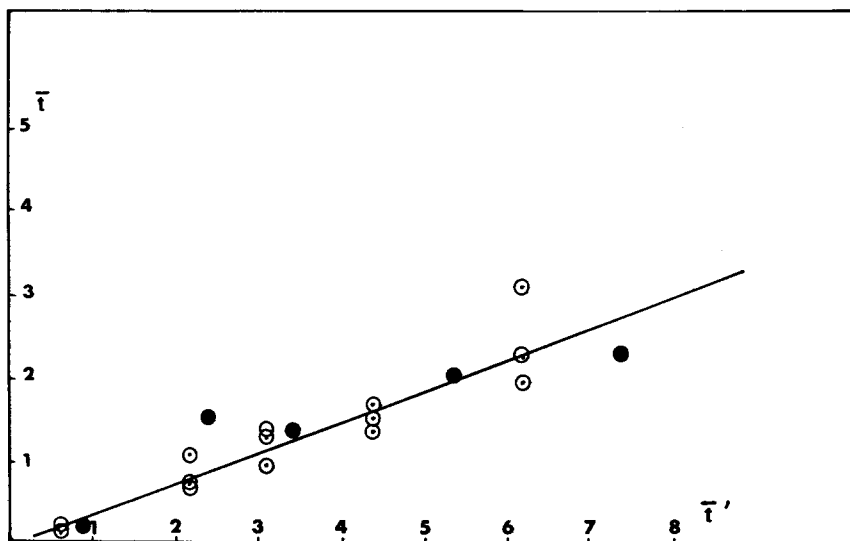


Fig. 4. Influence of temperature on the grafting of butadiene: (○) -60°C; (●) +30°C.

The polystyryl carbanion is a more efficient grafting agent than the polybutadienyl one at +30°C, since the value of m_s is 0.51 ± 0.04 . It has already been noted that the grafting yield \bar{l} , which is the number of grafted chains on one backbone, is an arbitrary unit and that the percentages of chlorine substitution may be of interest. With a molecular weight \bar{M}_n of 33,000 for PVC, we have

$$\bar{s} = \% \text{ of chlorine substitution} = 0.19 \bar{l}$$

Table VIII and Figure 5 show that the grafting is linear up to chlorine substitution percentage as high as 13% (which corresponds to one substituted atom of

TABLE VIII
Grafting Ratios of Polybutadienes on PVC Backbones and Corresponding Amount of Chlorine Substitution

No.	l'	l	\bar{s}'	\bar{s}
PBI 1	0.38	0.02	0.072	0.004
PB 25	0.48	0.15	0.091	0.028
PBIII 3	0.86	0.275	0.163	0.052
PBIII 4	0.91	0.42	0.173	0.080
PBI 2	1.15	0.28	0.218	0.053
PBIII 5	1.93	0.62	0.367	0.118
PB 50	2.16	0.72	0.410	0.137
PB I 3	2.32	1.04	0.430	0.198
PB II 1	2.59	0.82	0.49	0.156
PB 70	3.11	1.35	0.59	0.256
PB I 4	3.74	1.80	0.71	0.342
PB 701	4.38	1.33	0.83	0.252
PB III 6	4.50	1.60	0.86	0.304
PB II 2	4.94	2.10	0.94	0.395
PB I 5	5.67	2.43	1.08	0.462
PB 75	6.15	2.30	1.17	0.437
PB II 3	6.30	2.44	1.20	0.463
PB II 4	7.89	2.90	1.50	0.552
PB I 6	9.48	3.70	1.80	0.704
PB II 5	16.17	6.81	3.35	1.29
PB II 6	66.6	29.2	12.7	5.55

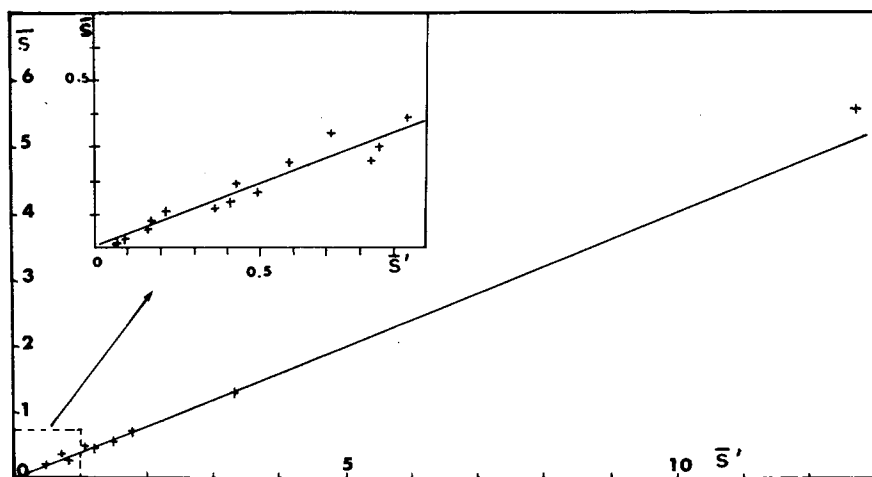


Fig. 5. Experimental average chlorine substitution \bar{S} vs. theoretical \bar{S}' : (a) blowup of graph for low values.

chlorine out of eight). As the molecular weight of the grafts are, respectively, 30,000–11,000 and 90,000 for the PB I, II, and III series, we cannot see any difference in grafting reactivity with the molecular weight of the grafting carbanion. The chemical aspects will be discussed later more in depth.

The authors wish to thank Mrs. Gary for the GPC measurements. A part of this work was supported by a scientific research contract of the DGRST foundation and the Pechiney Progil Society, which we wish to thank for permitting the publication of this paper.

References

1. G. Lechermeier, C. Pillot, J. Gole, and A. Revillon, *J. Appl. Polym. Sci.*, **19**, 1979 (1975).
2. P. Rempp, *Colloque Copolymères Greffés et Séquencés*, Mulhouse, 1972, p. 1.
3. J. M. Guyon-Gellin, J. Gole, and J. P. Pascault, *J. Appl. Polym. Sci.*, in press.
4. G. Lechermeier and C. Pillot, to be published.
5. A. Essel, Ph.D. Thesis, Lyon, 1974.
6. M. Szwarc, *Carbanions, Living Polymers and Electron Transfer Process*, Interscience, New York, 1968.
7. B. M. Quenum, J. L. Grandaud, P. Berticat, and G. Vallet, *Chim. Anal.*, **53**, 629 (1971).

Received December 2, 1974