Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Anionic Grafting on Polyvinyl Chloride)

G. Lechermeier[a]; A. Revillon[a]; C. Pillot[a]
[a] Laboratoire Associé au CNRS No. 199, Institut National des Sciences Appliquées, Villeurbanne, France

To cite this Article Lechermeier, G. , Revillon, A. and Pillot, C.(1978) 'Anionic Grafting on Polyvinyl Chloride)', Journal of Macromolecular Science, Part A, 12: 2, 285 — 299

To link to this Article: DOI: 10.1080/00222337808061376

URL: http://dx.doi.org/10.1080/00222337808061376

J. MACROMOL. SCI.–CHEM., A12(2), pp. 285-299 (1978)

Anionic Grafting on Poly(vinyl Chloride)

G. LECHERMEIER, A. REVILLON,* and C. PILLOT

Laboratoire Associé au CNRS No. 199
Institut National des Sciences Appliquées
69621 Villeurbanne, France

ABSTRACT

The grafting on poly(vinyl chloride) by carbanionic deactivation of a living polymer involves two types of reactions: a nucelophilic substitution (SN_2) and an elimination (E_2). Under the experimental conditions, of our study, we did not observe metallation of the poly(vinyl chloride) chain. The influence of different parameters on the ratio E/S of the two reactions has been studied. The substitution is enhanced when the basicity of the carbanion is decreased. Higher temperatures favor the elimination, which might be due to the relative change in the nature of the different ionic species. The appearance of conjugated double bonds, the electroattractive character of which makes the hydrogen atom in the α position of the C–Cl bond labile, favors autoacceleration of the elimination reaction. The shorter the living chain, higher the yield in substituted product. Steric hindrance of the random coils of PVC and living polymer also plays an important role.

---

*Present address: L. A. 199, CNRS, 79, Boulevard du 11 Novembre 1918, 69626 Villeurbanne, France.

INTRODUCTION

Graft and block copolymers are compounds whose synthesis is well known. Yet, few graft and block copolymers of PVC have been reported. We have developed a method of grafting on PVC leading to well defined copolymers in order to study the effects of the chemical structure on the morphology and through that, on the mechanical properties of the material.

The synthesis of graft copolymers by carbanionic deactivation was proposed by Rempp and al. [1], who allowed the esters or halide groups of a macromolecular chain to react with a living polymer:

$$\sim\!\sim\!\sim B^- + R\!-\!\!-\!X \longrightarrow \sim\!\sim\!\sim B\!-\!\!-\!R + X^- \qquad (1)$$

This substitution reaction (S) [Eq. (1)] generally competes with an elimination reaction (E) [Eq. (2)] which evolves hydrochloric acid and leads to the appearance of a double bond:

$$\sim\!\sim\!\sim B^- + \;\rangle CH\!-\!\overset{|}{\underset{|}{C}}\!-\!X \longrightarrow \sim\!\sim\!\sim BH + \;\rangle C\!=\!C\langle\; + XH \qquad (2)$$

The extent of the two above reactions depends on various factors, including basicity of the carbanion, steric effects, mesomeric effects of the substituents, nature of the counterion, solvent, and temperature.

A SN_1 monomolecular mechanism in two steps takes place chiefly in polar solvents (H_2O, H_2O plus alcohol . . .) since the first step is a heterolytic scission. Other effects may affect these mechanisms, such as nature of the halogen or nature of the alkyl group.[2].

When the reaction is performed in an aprotic solvent of low polarity (for instance THF, dielectric constant 11 at -60°C) and when a nucleophilic attack of a chlorine atom on a secondary carbon is involved (PVC for instance), the bimolecular mechanism is the most probable.

Roth, Rempp, and Parrod suggest such a mechanism for the action of different bases (phenylisopropylpotassium) on PVC. This secondary elimination reaction takes place as proved by the appearance of conjugated double bonds. The relative extent of the two reactions depends on the basicity of the carbanion [3, 4]. The yields of graft copolymers are not constant and make necessary removal of the homopolymer [5]. Despite the secondary reactions, this grafting process has often been used to modify the PVC: either to increase its stability [6] or to change its mechanical properties [7].

In a bimolecular process, where a transition state between reactants and products occurs, Gould [8] notes that the polarity of the solvent is very important. The rate of substitution decreases when the dielectric constant increases. This effect is stronger on the rate of elimination, owing to the higher dispersion of the charge on the activated complex. The E/S ratio decreases when the solvent polarity increases. This is also in agreement with references on the action of carbanions on a chlorinated polymer [4].

The dieclectric constant of the medium decreases when the temperature increases, which favors the elimination. Yet, this effect is relatively weak and not unique, since for the THF, the dielectric constant changes from 11 to 8.2 between -60 and 0° C. The equilibrium between the various ionic species is affected by the change of temperature, as is the reactivity of the carbanions [9]. The carbanion, in presence of metal ions such as alkali metal ions, may exist under different states: free ions, tight or loose ion pairs, or aggregates [9]. Free ions which are generally of higher reactivity may be considered to be of a higher basicity than ion pairs. Equilibrium between free ions and pairs depends on temperature, nature of the metal counterion, and concentration [10].

The E/S ratio increases with the basicity of carbanion [8]. This basicity is higher when the substituent is of low electroattractive character or when it is resonance-stabilized. It has been observed [1] that for the series phenylisopropyl, methylstyryl, styryl, the amount of dehydrochlorination varies with the number of methyl substituents (+I effect). In the series of carbanions with two phenyl groups, only the substitution reaction has been evidenced (-I effect) as the phenyl rings stabilize the carbanion and lower its reactivity [3].

EXPERIMENTAL

Synthesis

The general scheme is as follows: synthesis of a monofunctional living polymer with initiation by n-butyllithium in THF; addition of the living polymer to a solution of PVC in THF; precipitation of the reactive mixture in methanol and drying under vacuum (10^{-4} Torr).

The methods of preparation of the reactants are those usually used in anionic polymerization and have been already described [11].

For the synthesis of graft copolymers, the general scheme above has been used in two different ways. The first one is a multistep process A (Fig. 1). The living polymer is prepared at low temperature in the first reaction which is sealed to the flask containing the PVC solution. After degassing, the living polymer is poured into this flask by the means of a breakseal. In the second process B (Fig. 2), the reaction is performed on a line allowing the purification

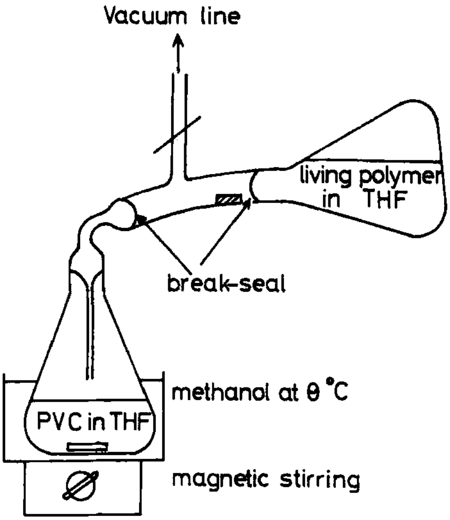


FIG. 1. Synthesis of graft copolymers by process A.

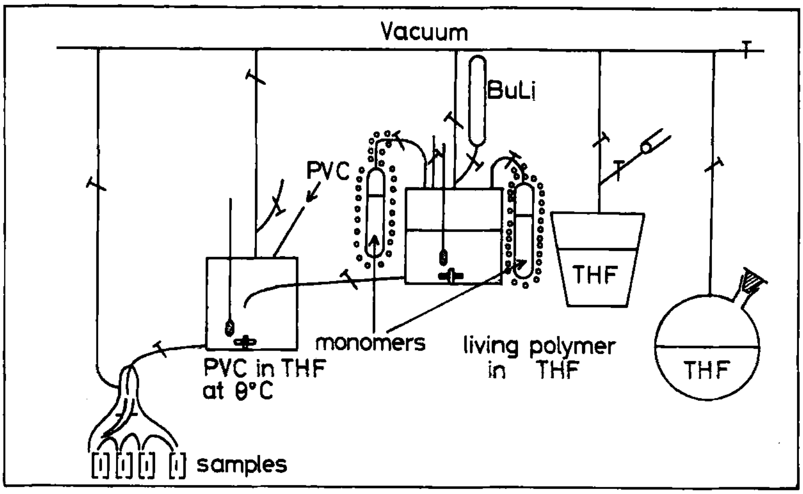


FIG. 2. Synthesis of graft copolymers by process B.

of solvent, the preparation of living homopolymer or block polymer, the addition of increasing amount of the latter, and the sampling itself. Two polymer chains were used as grafts: polystyrene (PS) and polybutadiene (PBd). The living polymer is either a homopolymer of PS of PBd or a block copolymer with some units of diphenylethylene, butadiene, or ethylene oxide. The code refers to the nature of the main compound of the graft (S or B).

Analytical Methods

The products were analyzed by several techniques: selective extraction, osmometry, gel-permeation chromatography (GPC) with a single or dual detection. The efficiency of these methods was studied statistically [12, 13].

The standard deviations σ are similar, yet the GPC dual detection technique has a higher accuracy and is used when possible (presence of UV absorbent). The following parameters were determined: overall composition of the reactive mixture (weight percentage of PVC and polymer to be grafted present as copolymer as well as homopolymer); true composition of the copolymer (percentage of PVC backbone and of grafted B or S type polymer); number-average molecular weight of PVC, $\overline{M}_n$ (PVC); number-average molecular weight of grafts $\overline{M}_n$(g); average number of grafts per PVC chain $\overline{t}$; average number of living polymer chains added per chain of PVC, $\overline{t}'$; efficiency of grafting R (fraction of grafted living polymer).

Additional UV characterization was carried out by use of a Cary 14 spectrophotometer.

RESULTS AND DISCUSSION

Several carbanions were reacted by process A and B on a given mass process PVC supplied by Rhône Poulenc Polymères Society. THF was the only reaction solvent. The conditions are summarized in Table 1. Each line represents a series of reactions with the same grafting end at different grafting ratios E.

Influence of the Molecular Weight of the Graft

The systematic study of this effect was made with polybutadienyl grafting anions which appear in the upper part of Table 1 of molecular weight varying from 4,200 up to 90,000. By plotting $\overline{t}$ versus $\overline{t}'$

TABLE 1. Conditions of Synthesis and Analysis

No.	Terminal anion	Number-average MW of graft $\overline{M}_n$(g)	Temperature of reaction (°C)	Synthesis process	Analytical method	Average number of grafts per PVC chain $\overline{t}$	Grafting efficiency R
PB IV	Butadienyl	4,200	-60	B	GPC single	4-42	0.44 ± 0.02[a]
PB II	"	11,000	-60	B	extraction	0.8-22	0.448 ± 0.007
PB I	"	30,000	-60	B	"	0.28-3.7	0.42 ± 0.04
PB III	"	90,000	-60	B	"	0.27-1.6	0.35 ± 0.05
PB V	Oxanion	6,200	30	A	GPC single	0[b]	0
PS	Styryl	5,500	-60	A	GPC dual	0.2-6.2	0.60[c]
PS I	"	18,000	30	B	GPC dual	0.56-8.95	0.53 ± 0.07
PS III	Butadienyl	15,000	30	B	GPC dual	0.27-1.6	0.39 ± 0.06
PS II	Diphenylethylenyl	20,000	30	B	GPC dual	0.17-3.35	0.55 ± 0.03
PS IV	"	29,000	-60	A	extraction	2.5	0.78[c]
PS V	"	3,000	-60	A	"	31	0.60[c]

[a] Probable error at a confidence value of 90%.
[b] Very slow reaction (24 hr).
[c] When using the process A, efficiency not calculated from $\overline{t}$ ($\overline{t'}$) curve.

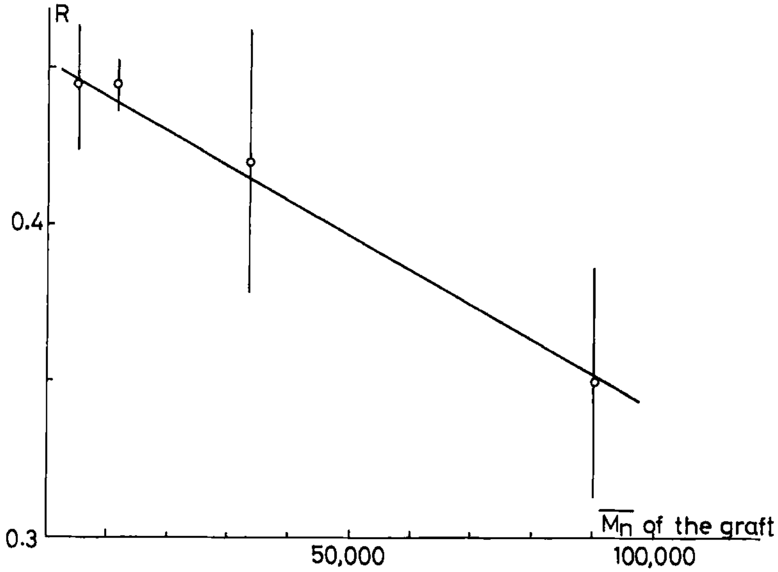


FIG. 3. Variation of the grafting efficiency R as a function of the molecular weight of the polybutadiene grafts at -60°C.

for each series of graft copolymers, the efficiency R is determined by means of a linear regression. The decrease of R when $M_n(g)$ increases is larger than the experimental error (Fig. 3). It may be thought that this decrease is due to the increasing size of the random coil of the graft which reduces the probability of approach of the reactants. Another factor to be considered is the increasing incompatibility of the polymers with increasing molecular weight.

Influence of the Grafting Ratio on the Grafting Efficiency

This effect has been observed with low molecular weight polybutadienes (PB IV) which allow high grafting ratios $\overline{t}$ to be reached. The representative curve of $\overline{t}$ versus $\overline{t}'$ indicates that the efficiency tends to decrease at high values of $\overline{t}'$ (Fig. 4). The slope of the regression line has been calculated only with the first values, since the whole set of experimental data leads to a too low value in the Snedecor test. The same tendency is observed with polystyrene-diphenylethylenyl grafts of PS II and PS IV polystyrene experiments: the grafting

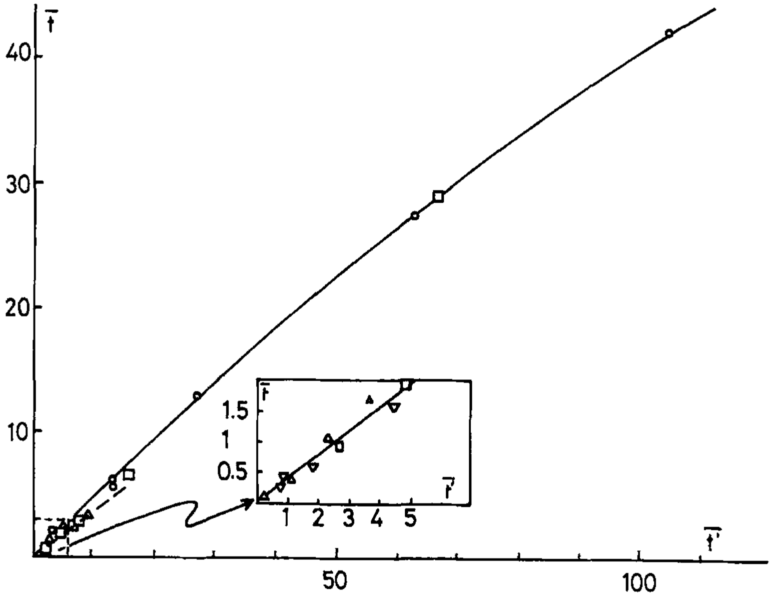


FIG. 4. Effective average grafting ratio ($\bar{t}$) vs. the number of carbanions added ($\bar{t}'$) per PVC chain for four series of polymers of various molecular weights: (○) 4,200; (□) 11,000; (△) 30,000; (▽) 90,000.

TABLE 2. Correlation of the Grafting Efficiency R to the Basicity of the Anion and the Temperature of Reaction

Decreasing basicity	Half-wave potential (V)	Grafting efficiency	Temperature (°C)
Polybutadienyl	2.59	0.448 ± 0.007	-60
		0.39 ± 0.006	
Polystyryl	2.39	0.6[a]	-60
		0.53 ± 0.07	+30
Diphenylethylenyl	2.14	0.69[a]	-60
		0.55 ± 0.03	+30
Oxanion	-	0	+30

[a] Efficiency not calculated from $\bar{t}(\bar{t}')$ curve.

efficiency varies from 0.78 down to 0.60 as the grafting ratio changes from 2.5 up to 31.

It appears that the presence of a high number of grafts on the backbone inhibits the attack of the carbon linked to the chlorine atom. It is well known that in the synthesis of star-shaped polystyrene, it is difficult to have more than four branches. The first two chains react rapidly, then the accessibility of the other reactive sites is decreased by the repulsive effect of identical chains and by the diffusion of polymer in polymer-rich regions [14]. Autoretardation of this type has also been mentioned [15] for the reaction of organolithium compounds on poly(methyl methacrylate), attributed to steric hindrance and the repulsive electrostatic effect of already substituted neighboring units of methyl methacrylate MMA for ester sites of MMA.

Influence of the Carbanion and of the Temperature

The results of the two effects are reported in Table 2. The higher the basicity of the carbanion is, the lower the efficiency. For instance, significant substitution is observed on use of living polymers just terminated by few units of 1,1-diphenylethylene, since the corresponding carbanion is highly stabilized by its two phenyl rings.

The lower the temperature is, the higher the grafting efficiency. This may receive two explanations: the dielectric constant of the solvent increases at low temperature, so that the rate of elimination is much decreased than the substitution one. Moreover, as the equilibrium between the various ionic species is modified, the increase in the free ions concentration favors the substitution.

Oxanion-terminated grafting species are apart. The reaction is made with an anion the basicity of which is much lower and there is no grafting at all. Either living species are so different than with carbanion or the potential of the anion is too low for the substitution reaction itself [16].

Study of the Dehydrochlorination Reaction

The elimination reaction leads to double bonds on the PVC backbone together with a HCl elimination.

The double bond concentration was studied by UV absorption spectra obtained with a Cary 14 spectrophotometer.

The spectra of the series of copolymers with grafts of 4200 molecular weight are shown in Fig. 5.

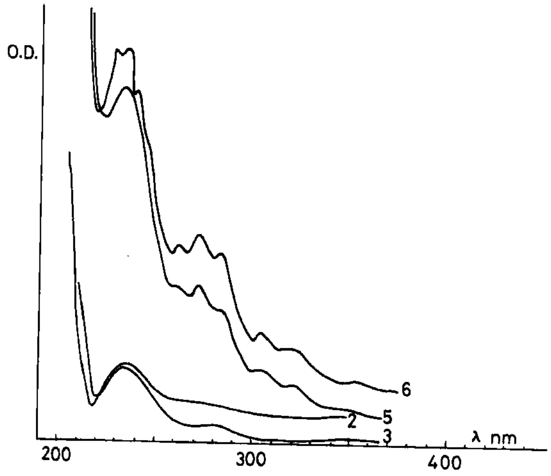


FIG. 5. UV spectra of butadiene copolymers (series IV, $\overline{M}_n$ of the graft = 4,200) at different grafting ratios $\overline{t}$ (2) t = 4; (3) t = 13; (5) t = 28; (6) t = 42.

The band indexation is not simple, since we observe partial overlap of the individual peaks and increase of bands width with substituent, or isomeric effects. We have used the works of Daniels [17] and Abbas [18] for the indexation of the peaks. It is noteworthy that we obtain effects of living species of different reactivities [19].

The calculation of the concentration in polyene is difficult, since the diene corresponds to one peak, the triene to three, and the higher conjugated products to four peaks. We can, however, use the literature values of absorption coefficient to obtain a semiquantitative approach to the phenomenon.

Table 3 gives the value of the absorption coefficients and the corresponding wavelengths of the peaks from literature and from our study. These values enable us to calculate the individual concentration of the different polyenes.

TABLE 3. Absorption Maxima for Different Lengths of Conjugated Double Bond Sequences

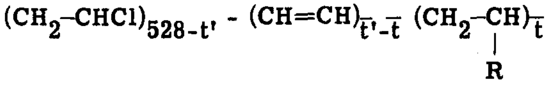
Number of conjugated double bonds	λ (nm)			Absorption coefficient ϵ (Daniels and Rees)[b]
	Abbas[a]	Daniels and Rees[b]	This work	
2			235	20,000[c]
3	288	240, 248, $\underline{257}$, 268	260-272	42,700
4	308	267, 278, $\underline{290}$, 304	305	78,600
5	324	279, 290, 303, $\underline{317}$, 334	322	121,000
6	340	300, 313, 328, $\underline{344}$, 364	355	138,000
7	364	316, 332, 350, $\underline{368}$, 390	360	177,100
8	388	332, 349, 367, $\underline{386}$, 410	385	210,000
9	412	345, 363, 380, $\underline{404}$, 430	408	242,800
10	434	358, 376, 397, $\underline{420}$, 447	430	275,600

[a] Data of Abbas and Sorvik [18].
[b] Data of Daniels and Rees [17].
[c] Assumption.

These individual concentrations, as well as the overall double bond concentrations are reported in Table 4.

We can now calculate the proportion α of conjugated double bonds over the total double bonds concentration.

The parent PVC has a molecular weight of 33,000; that means the monomer unit is repeated 528 times. The number of carbanion added per chain of PVC is $\bar{t}'$. The number of grafts is $\bar{t}$. The general formula is then



$$(CH_2{-}CHCl)_{528-t'} - (CH{=}CH)_{\bar{t}'-\bar{t}}\ (CH_2{-}\underset{\substack{|\\R}}{C}H)_{\bar{t}}$$

TABLE 4. Concentration of Conjugated Double Bonds (Created by the Elimination Reaction) for Each Length n of Conjugated Sequence

	Concn of conjugated double bonds (mole/liter × 10^4)			
	PB IV 3, t = 13	PB IV 5, t = 28	PB IV 6, t = 42	PB V, t = 0
n = 2	0.4	2.7	3	3.25
n = 3	-	0.98	0.51	1.45
n = 4	-	0.089	0.11	0.7
n = 5	-	-	0.058	0.43
n = 6	-	-	-	0.25
n = 7	-	-	-	0.19
n = 8	-	-	-	0.124
n = 9	-	-	-	0.07
n = 10	-	-	-	0.04
Total	0.4	3.27	3.68	6.5

and the molecular weight is calculated as

$$\overline{M}_n = 62.5\ (528 - t') + 26\,(\overline{t}' - t) + 4227\overline{t}$$

as the molecular weight of grafted chains is 4227.

The concentration in grafted copolymer is c (the ungrafted polybutadiene has been selectively extracted). The overall concentration in double bonds is expressed as c $(\overline{t}' - \overline{t})/\overline{M}_n$, and α is obtained as we already know the conjugated double bonds concentration. The calculations are reported in Table 5.

With an oxanion chain end, there is only elimination.

The UV spectrum presents numerous absorption bands due to numerous polyenes in the PVC backbone, from 2 to 10 conjugated double bonds (Fig. 6). In Table 5, we can see that we have 36% of conjugated bonds. This is a very high proportion relative to the other carbanions, where α is between 8 and 16%.

TABLE 5. Proportion α of Conjugated Double Bonds over the Total Concentration of Double Bonds

	PB IV 3	PB IV 5	PB IV 6	PB V
$\bar{t}$	13	28	42	0
$\bar{t}'$	29	63	104	17,3
$\bar{M}_n$	86,554	148,900	205,600	32,400
C (g/l)	2.9	8.7	8.8	3.4
Double bonds concn (mole/l.)	5.3×10^{-4}	20.4×10^{-4}	26.5×10^{-4}	17.8×10^{-4}
Conjugated double bonds concn (mole/l.)	0.4×10^{-4}	3.27×10^{-4}	3.68×10^{-4}	6.5×10^{-4}
α	0.08	0.16	0.14	0.36

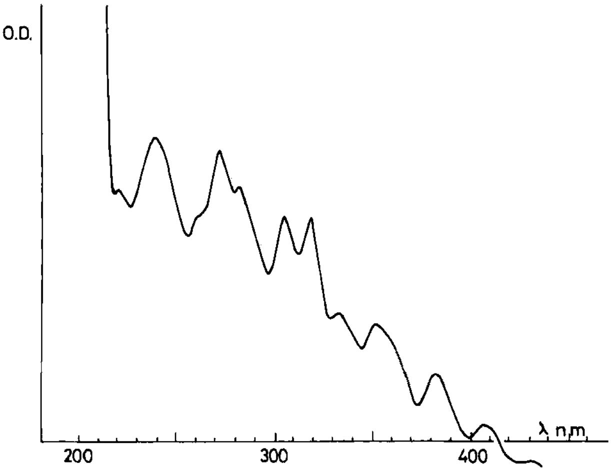


FIG. 6. UV spectrum of an oxanion-terminated polybutadiene-grafted polymer ($\bar{t}'$ = 17.3).

Since there is no competition between elimination and substitution, the formation of conjugated double bonds (n = 2) must induce (by -I effect) the dehydrochlorination of the neighboring unit. The elimination reaction is then autoaccelerated, and polyenes of higher conjugation are obtained.

ACKNOWLEDGMENT

This work has received partial support from the Delegation Generale à la Recherche Scientifique et Technique [20].

REFERENCES

[1] J. Roth, P. Rempp, and J. Parrod, C. R. Acad. Sci. (Paris), 251, 3356 (1960).

[2] C. K. Ingold, in Structure and Mechanism in Organic Chemistry, 2nd ed., C. K. Ingold, Ed., Cornell Univ. Press, Ithaca, N. Y., 1969.

[3] A. Dondos and P. Rempp, C. R. Acad. Sci. (Paris), 254, 1064 (1962).

[4] P. Rempp, J. Parrod, G. Laurent, and Y. Gallot, C. R. Acad. Sci. (Paris), 260, 903 (1963).

[5] Y. Gallot, P. Rempp, and J. Parrod, J. Polym. Sci. B, 1, 329 (1963).

[6] J. D. Nichols, J. Polym. Sci. Polym. Letters Ed., 11, 705 (1973).

[7] Y. Minoura, H. Hironaka, T. Kasabo, and Y. Ueno, J. Polym. Sci. A-1, 6, 2773 (1968).

[8] E. S. Gould, in Mechanism and Structure in Organic Chemistry, Holt, Rinehart and Winston, New York, 1966.

[9] M. Szwarc, Carbanions, Living Polymers and Electron Transfer Processes, Interscience, New York, 1968.

[10] D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, J. Phys. Chem., 69, 612 (1965).

[11] A. Essel, Thesis 235, Université de Lyon, France, 1974.

[12] G. Lechermeier, C. Pillot, G. Golé, and A. Revillon, J. Appl. Polym. Sci., 19, 1979 (1975).

[13] G. Lechermeier, A. Revillon, and C. Pillot, J. Appl. Polym. Sci., 19, 1989 (1975).

[14] H. Eschweg, M. L. Hallensleben, and W. Burchard, Makromol. Chem., 173, 235 (1973).

[15] J. C. Gallin, Modifications Topochimiques de Polymères. Report of DGRST contract No. 73.7.1130 (1975).

[16] P. D. Lassale, Thesis, Université de Paris VI, CNRS No. A0 7661.
[17] V. D. Daniels and N. H. Rees, J. Polym. Sci. Polym. Chem. Ed., 12, 2115 (1975).
[18] K. B. Abbas and E. M. Sorvik, J. Appl. Polym. Sci., 19, 2991 (1975).
[19] M. Szwarc, Ions and Ions Pairs in Organic Reactions, Wiley-Interscience, New York, 1974, p. 203.
[20] G. Lechermeier, Thesis, Université de Lyon, France, I-DE. 76.006, 1976.