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

Vinyl Chloride-Vinyl Bromide Copolymers

A. Michel[a]; G. Schmidt[a]; A. Guyot[a]
[a] C.N.R.S. Institut de Recherches sur la Catalyse, Villeurbanne, France

To cite this Article Michel, A. , Schmidt, G. and Guyot, A.(1973) 'Vinyl Chloride-Vinyl Bromide Copolymers', Journal of Macromolecular Science, Part A, 7: 6, 1279 — 1296

To link to this Article: DOI: 10.1080/10601327308060498

URL: http://dx.doi.org/10.1080/10601327308060498

J. MACROMOL. SCI.—CHEM., A7(6), pp. 1279-1296 (1973)

Vinyl Chloride-Vinyl Bromide Copolymers

A. MICHEL, G. SCHMIDT,* and A. GUYOT

C.N.R.S.
Institut de Recherches sur la Catalyse
Villeurbanne, France

ABSTRACT

Radical copolymerization kinetics of vinyl chloride (VC) and vinyl bromide (VB) lead to the following reactivity ratios

$$r_{VC} = 0.825 \qquad r_{VB} = 1.05$$

Vinyl bromide acts as a chain transfer agent, more powerful than vinyl chloride, the transfer constant for VC radicals being 8.5×10^{-3} at 40°C. Neither thermal nor ionic degradation produce controlled distribution of short diene sequences in the copolymer. In the ionic process initiated with LiCl or LiBr in dimethylformamide solution, substitution of halogen atoms as well as acid elimination takes place.

INTRODUCTION

Because polyvinyl bromide (PVB) is far less stable than polyvinyl chloride (PVC), copolymers with high vinyl chloride content

---

*Deceased October 1972.

may be considered as polymer models with weak points for the study of the degradation of PVC. Braun and Thallmaier have concluded that the first step in the thermal decomposition of these copolymers requires at least two neighboring VB units [1]. Their sequence distribution calculation was based upon the assumption of an equal reactivity of the two monomers versus the two kinds of radicals ($r_1 = r_2 = 1$). Our purpose was to use copolymers to prepare, after selective dehydrobromination, polymers with a known number and distribution of double bonds sequences in order to study their ozonolysis, as described in another paper [2]. The present work includes a kinetic study of the radical copolymerization for the determination of the actual reactivity ratio, the calculation of the sequence distribution of the first steps of the thermal degradation, and a study of the ionic degradation initiated by weak bases (LiCl, LiBr) in dimethylformamide. It was concluded that in both cases the dehydrobromination is not selective and long sequences of double bonds are generated.

COPOLYMERIZATION

The kinetic study of radical copolymerization initiated at 40°C by cyclohexylpercarbonate has been carried out in solution in dichloroethane. The solvent being used as a concentration reference and the gas chromatographic analysis of samples chosen at convenient time interval allows, according to a method previously described [3], the drawing of conversion curves of the individual monomers from which the initial rates may be accurately derived. The charges of the initial solutions of the experiments are reported in Table 1 together with the initial composition of the copolymers. After a limited conversion (less than 10%) the copolymers were precipitated in methanol, washed, and dried under vacuum at room temperature. Their limiting viscosity number, measured in tetrahydrofurane solution at 25°C, are also reported in Table 1.

The results were used to draw a Fineman-Ross [4] plot which was a straight line over the whole range of monomer feed compositions, indicating no deviation from the Lewis and Mayo copolymerization theory. The reactivity ratios $r_{VC} = 0.825$ and $r_{VB} = 1.05$ were obtained. These reactivity ratios are not exactly equal but are very close to 1, and thus no drift in the copolymer composition is to be expected, even after high conversion has been reached. The composition of the copolymers has been checked quite satisfactorily by elemental analysis.

The molecular weight decreases markedly when the VB content of the copolymer increases so that it may be assumed that this monomer acts as a rather powerful transfer agent.

TABLE 1. Solution Copolymerization of Vinyl Chloride (VC) and Vinyl Bromide (VB)

Reactor charge (moles)			$\frac{VB}{VC}$	$\frac{dVB}{dVC}$	
VB	VC	Solvent	initial	initial	η
0.426	0.208	5.25	2.048	2.277	8.0
0.245	0.222	5.15	1.102	1.238	8.0
0.0785	0.320	5.06	0.245	0.289	12.1
0.030	0.515	5.15	0.0583	0.069	18.7
0.0155	0.616	5.25	0.0252	0.0291	22.2
0.0097	0.78	5.63	0.0125	0.0155	26.5

Suspension copolymerization experiments have been undertaken in order to obtain copolymers with a molecular weight comparable to that of commercial PVC. The initiator was again cyclohexylpercarbonate, and the protective colloid system included a mixture of polyvinyl alcohol (0.4 part per 100 parts of monomer) and hydroxymethyl cellulose (0.1 part). The experiments were carried out at 40°C in a 1-liter autoclave (Ingenieur Bureau, Zurich) at a stirring speed of 300 rpm. The results are reported in Table 2. It may be observed again that the presence of vinyl bromide does not markedly affect the polymerization rate, but does cause a decrease in the molecular weight. It is well known that the molecular weight of PVC under bulk conditions is dependent only on the temperature and so is regulated by a transfer mechanism on the monomer. In these copolymerization experiments there are four transfer reactions involving two polymer radicals and two monomers, and the data are not sufficient to determine all the transfer constant involved. However, for mixtures with low VB content, most of the radicals are VC-ended radicals and it is possible, to a first approximation, to derive the transfer constant C_{CB} of this radical on the VB monomer from a plot of the inverse of the number-average degree of polymerization versus the molar ratio of VB on the whole monomer:

$$\frac{1}{\overline{DP}_n} = \frac{1}{(DP_n)_0} + C_{CB}\frac{[VB]}{[VB]+[VC]}$$

where $(DP_n)_0$ is the degree of polymerization of the PVC homopolymer prepared at the same temperature. From the viscosity data and the relationship recently proposed by DeVries et al. [4],

$$\eta_{THF}^{25^\circ C} = 1.63 \times 10^{-2} M_w^{0.76} \quad (cm^3/g)$$

it is possible to derive M_w. Assuming further the most probable distribution, $\overline{DP}_n$ is calculated from $\overline{M}_w/\overline{M}_n = 2$.

From the plot given in Fig. 1, $C_{CB} = 8.5 \times 10^{-3}$ is obtained. This value is markedly larger than that obtained for the transfer constant on monomer in VC homopolymerization, given as 1.94×10^{-3} by Park and Smith [5] in solution polymerization and as 1.03×10^{-3} by Danusso et al. [6] for bulk polymerization. The intercept of the line in Fig. 1 gives a rough estimate of this transfer constant as 0.82×10^{-3}, assuming that the growth of the polymer chains is essentially stopped upon transfer on monomer.

TABLE 2. Suspension Copolymerization of Vinyl Chloride (VC)-Vinyl Bromide (VB)

Monomer feed (moles)		Copolymer analysis (wt%)								
VB	VC	Br calc	Br found	Cl calc	Cl found	Duration (hr/min)	Conversion (%)	η	M_v	DP_n
0.334	2.795	14.62[a]	13.87[b]	45.63[a]	46.05[b]	6/5	77.4	73.2	63900	510
0.114	3.189	5.13[a]	5.34[b]	52.84[a]	52.89[b]	6/10	75.0	111.4	111100	890
0.036	3.234	1.68	1.61[c]	55.46[a]	55.31[b]	6/10	79.1	132.5	139600	1120
0.019	3.394	0.86	0.85[c]	56.08[a]	55.53[b]	4/45	61.6	133.9	141500	1133
0.0116	3.312	0.52	0.49[c]	56.33[a]	55.42[b]	4/45	61.0	138.8	148400	1190

[a] Calculated using reactivity ratios.
[b] From elemental analysis.
[c] From Br radioactivation analysis.

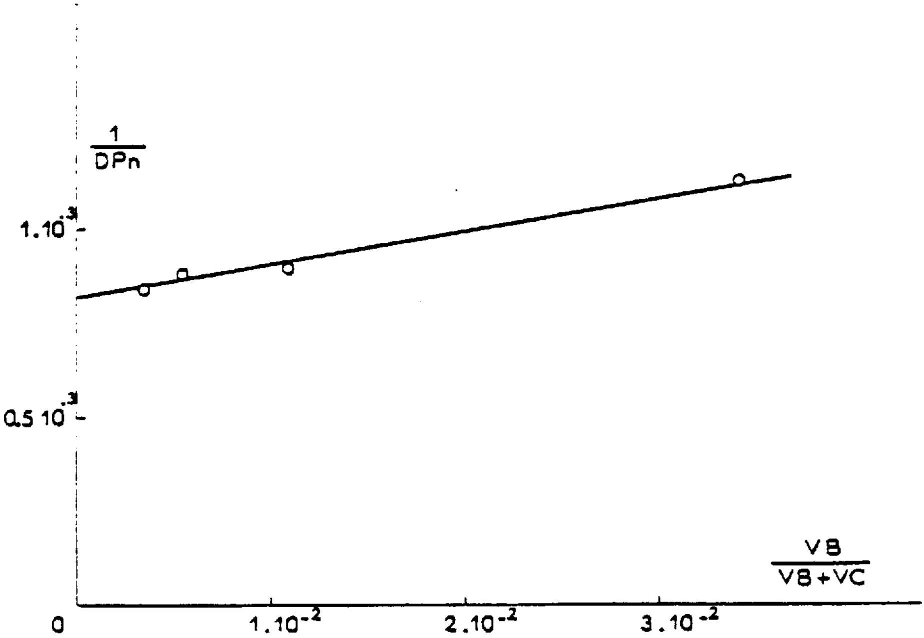


FIG. 1. Determination of the transfer constant of vinyl chloride ended radicals on vinyl bromide monomer.

A few of these copolymers have been used for the study of thermal or ionic degradation. The sequence distribution has been calculated from the above reactivity ratios, taking in account the slight drift of monomer mixture composition for high conversion copolymers. The results are reported in Table 3.

THERMAL DEGRADATION

Thermal dehydrohalogenation in an argon atmosphere has been studied in the 80-120°C temperature range by titration of the acids evolved with the differential conductimetric apparatus previously described [7]. A set of calibration experiment has shown that the increase of conductivity caused by HBr or HCl addition was identical. Typical results obtained with a few copolymers are shown in Figs. 2 and 3. Copolymers are less stable than PVC homopolymer. The copolymers prepared in solution are much less stable than copolymers, with higher bromine content prepared in suspension.

TABLE 3. Sequence Distribution of Vinyl Chloride (VC)-Vinyl Bromide (VB) Copolymers

Copolymer				Distribution (% of units) of sequence of length n											
No.	Polymerization	VC (mole %)	VB (mole %)	n	1	2	3	4	5	6	7	8	9	10	>10
A	Solution	97.1	2.9	VB	94.9	4.88	0.19								
				VC	0.087	0.169	0.246	0.319	0.387	0.45	0.51	0.566	0.618	0.606	95.98
B	Solution	93.4	6.5	VB	88.81	10.23	0.88	0.07							
				VC	0.43	0.81	1.14	1.42	1.65	1.85	2.02	2.16	2.26	2.35	83.90
C	Solution	77.6	22.3	VB	63.23	25.9	7.95	2.17	0.55	0.14	0.03				
				VC	5.25	8.10	9.36	9.62	9.27	8.57	7.71	6.79	5.89	5.04	24.37
D	Suspension	98.67	1.32	VB	97.7	2.26	0.039								
				VC	0.018	0.035	0.052	0.068	0.084	0.099	0.11	0.13	0.14	0.16	99.1
E	Suspension	95.9	4.1	VB	92.9	6.72	0.36	0.017							
				VC	0.17	0.33	0.47	0.61	0.73	0.83	0.93	1.02	1.10	1.18	92.61
F	Suspension	87.45	12.55	VB	78.97	17.58	2.94	0.44	0.06						
				VC	1.60	2.79	3.65	4.26	4.65	4.87	4.97	4.96	4.88	4.73	58.63

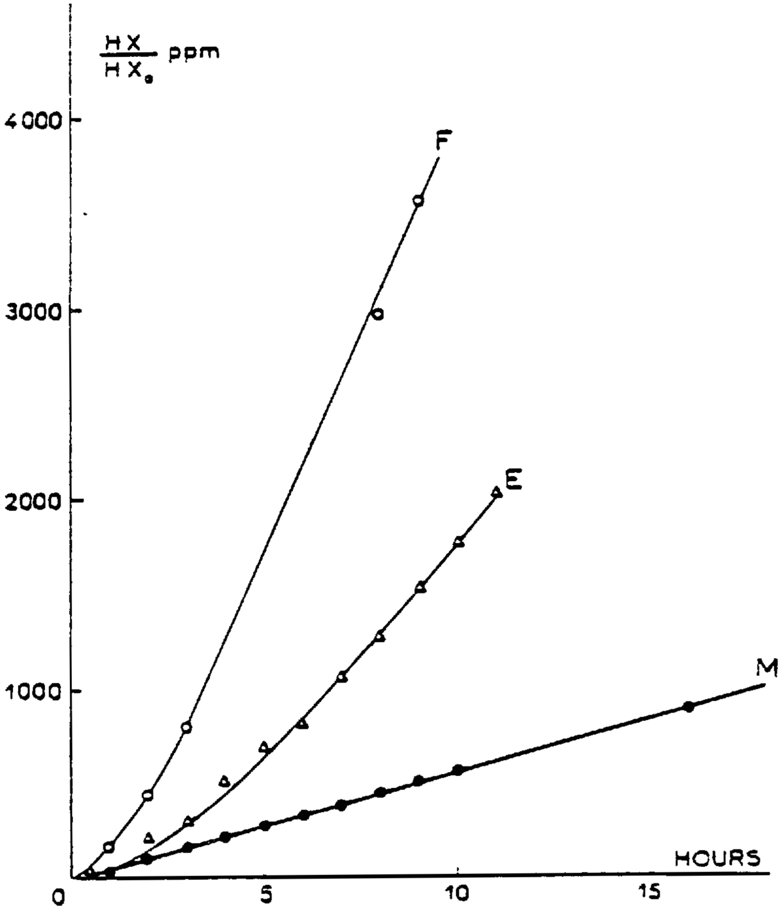


FIG. 2. Dehydrohalogenation ratio vs time at 135°C for solid copolymers (100 mg) E (suspension 4.1% VB) and F suspension 12.55% VB) compared with a commercial polyvinyl chloride homopolymer M.

This feature has been confirmed with other solution copolymers. After degradation the copolymers are strongly colored, and UV spectra show that long polyene sequences are formed. It is clear that dehydrobromination is not selective at these temperatures, and, as shown by the sequence distribution of the copolymers reported in Table 3, dehydrochlorination is certainly more important. The curve for Copolymer A

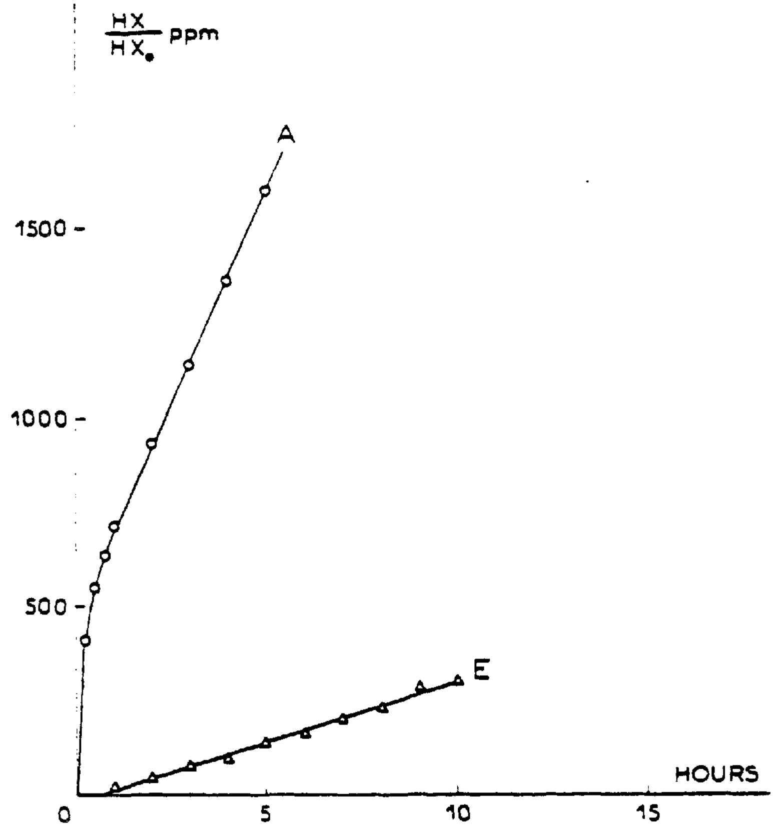


FIG. 3. Comparison of a solution Copolymer A (2.9% VB) and a suspension Copolymer E (4.1% VB) at 120°C. Dehydrohalogenation ratio vs time.

in Fig. 2 show a two-step process. Assuming selective dehydrobromination, the first step would account for about 1% of the theoretical HBr; this value show no correlation with the sequence distribution of VB units and, further, the coloration of the copolymer after 1 hr clearly indicates the presence of long polyene sequences. The results obtained at 80°C (Fig. 4) are again surprising because Copolymer B, with a higher VB content than Copolymer A, is the more stable. Again the plateau values reached after about 20 hr of degradation cannot be related with any feature of the sequence distribution.

Thus, even at very low temperatures, thermal degradation is by no means selective and fails to produce isolated double bonds in the

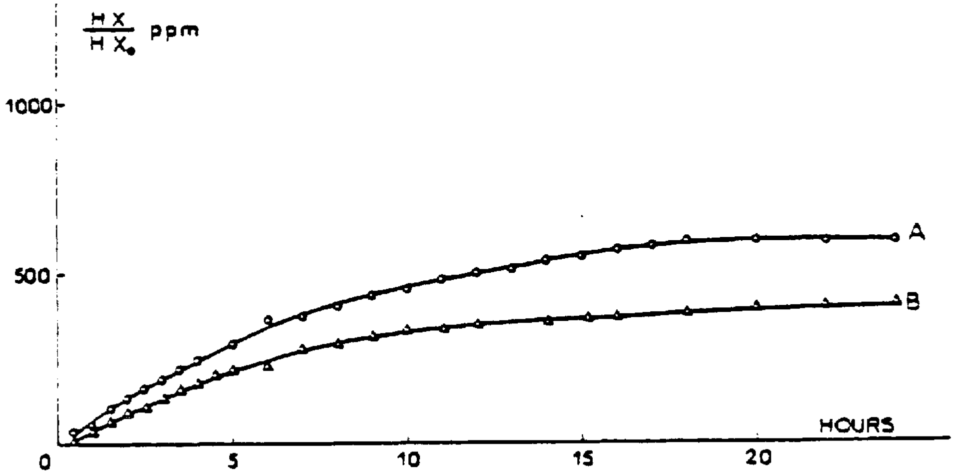


FIG. 4. Dehydrobromination ratio vs time at 80°C for solid Copolymers A (solution 2.9% VB) and B (solution 6.5% VB).

copolymer. It seems that the degradation rate cannot be related to the chemical composition of the copolymers. Most probably physical factors, such as the location of the glass transition temperature, the internal mobility of the copolymer at the temperature of the experiment, the morphology of the product, and the diffusion rate of the reactants, are more important in governing the degradation rate. The data reported here support this kind of statement, previously published about PVC homopolymer thermal degradation at low temperatures [7].

IONIC DEGRADATION

Following the work initiated by Roth et al. [8] on the ionic dehydrochlorination of PVC, and applied by Guenifrey et al. [9] to the selective dehydrobromination of chlorinated and brominated polybutadiene, attempts to obtain the selective dehydrobromination of VC-VB copolymers have been carried out. Solutions of polymer in purified dimethylformamide (0.16 mole of structural unit per liter) have been treated under dry nitrogen by LiBr or LiCl (0.5 to 1 mole/liter) for various times and at various temperatures. After precipitation with methanol or, occasionally, water, the dried copolymers have been studied by elemental analysis and UV-visible spectroscopy (apparatus: Cary 14).

TABLE 4. Ionic Degradation of Copolymer C (22.3% VB, 77.6% VC)

				Copolymer analysis		Weight percent of units		
Base	Conc (mole/liter)	T (°C)	Time (hr)	Cl (%)	Br (%)	VC	VB	—CH=CH—
			0	38.07	24.37	67.1	32.6	0.3
LiCl	1	30	8	43.6	14.27	81	19	-
			26	50.02	8.83	88.2	11.8	-
			47	51.40	7.51	90.4	10.0	
			55[a]	52.05	4.94	91.7	6.6	1.7
			55[b]	49.59	4.45	87.4	5.95	6.6
LiBr	1	30	8	37.1	24.28	65.4	32.5	2.1
			26	36.8	23.33	64.9	31.2	3.9
			47	38.4	23.93	67.7	32.0	0.3
			55[a]	39.0	23.53	68.7	31.5	-
			55[b]	38.45	22.81	67.8	30.5	1.7

[a] Polymer precipitated with methanol.

[b] Polymer soluble in methanol, precipitated with water.

TABLE 5. Ionic Degradation of Copolymer D (1.32% VB, 98.67% VC)

Base	Conc (mole/liter)	T (°C)	Time (hr)	Copolymer analysis		Weight percent of units		
				Cl (%)	Br (%)	VC	VB	—CH=CH—
			0	55.3	1.61	97.50	2.15	0.35
LiCl	0.5	30	12	55.8	0.81	98.4	1.1	0.5
			24	55.36	0.53	97.6	0.7	1.7
			52	53.78	0.34	94.8	0.5	4.7
			100	52.12	0.21	91.9	0.4	7.8
LiCl	1	50	3	54.65	0.4	96.3	0.5	3.1
			6	54.34	0.2	95.8	0.3	3.9
			24	53.21	0.06	93.8	0.08	6.1
			48	54.48	0.04	96.0	0.05	3.9
LiBr	0.8	50	8	54.13	2.50	95.4	3.3	1.2
			19	53.45	3.45	94.2	4.6	1.2

[a] From Br radioactivation analysis.

TABLE 6. Ionic Degradation of Copolymer F (12.4% VB, 87.6% VC)

Base	Conc (mole/liter)	T (°C)	Time (hr)	Copolymer analysis		Weight percent of units		
				Cl (%)	Br (%)	VC	VB	—CH=CH—
LiCl	0.5	30	0	46.05	13.87	81.2	18.6	0.27
			6	49.71	9.29	87.6	12.4	-
			24	51.35	6.68	90.5	8.9	0.54
			52	53.28	4.23	93.9	5.7	0.42
			100	54.40	1.91	95.9	2.6	1.55
LiCl	1	50	3	52.07	4.74	91.8	6.5	1.75
			6	53.01	3.07	93.4	4.1	2.5
			24	54.27	1.61	95.7	2.15	2.2
			48	53.75	0.90	94.7	1.2	4.1

Knowledge of the chlorine and the bromide content allows calculation of the weight percent of undegraded VC and VB units, respectively. The number of degraded —CH=CH— units is calculated by difference to 100. The results of elemental analysis are reported in Tables 4, 5, and 6, for copolymer C, D and F respectively.

Dehydrobromination is never selective, and hydrochloric acid is eliminated together with HBr. Further, the main reactions seem to be the substitution of chlorine with the Br ions from LiBr and of bromine with the Cl ions of LiCl. This is most visible in the case of Copolymer B which was treated at 30°C with the higher concentration of LiCl. The acid elimination remains limited although the copolymer becomes colored. The coloration process is dependent on the nature of the base, the temperature, and the time. At 30°C, with LiBr, the reaction medium becomes yellow, then orange, red, and finally dark brown, while with LiCl the same colors are observed at first but the final color is red-brown. At 50°C (Copolymer D) the color, at first yellow, turns to brown-purple with LiBr and becomes from pink to purple with LiCl. At 70°C, with LiBr, the same copolymer rapidly becomes brown, then dark and insoluble.

As shown by the spectra in Figs. 5 and 6 of Copolymer D degraded

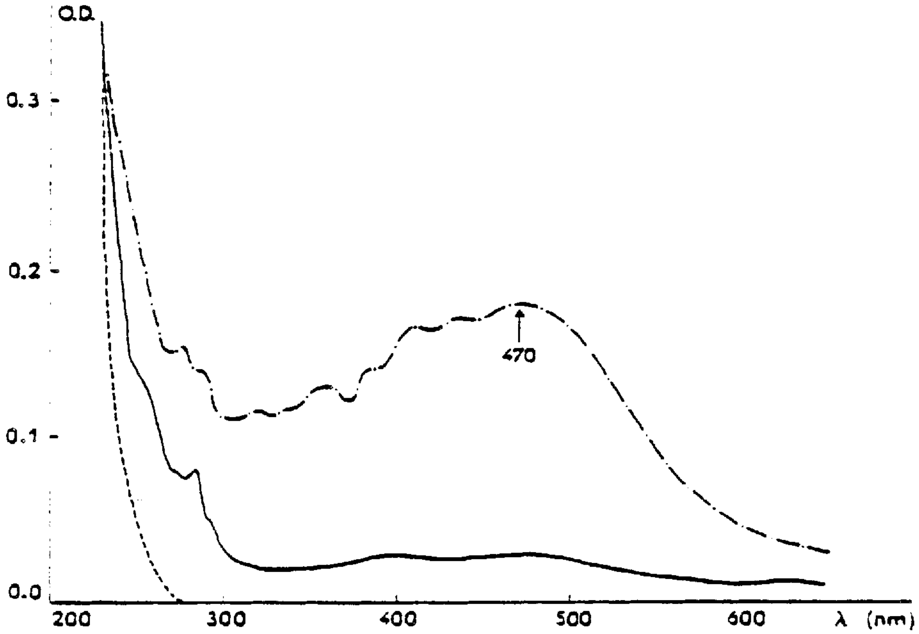


FIG. 5. UV-visible spectra of Copolymer D degraded at 30°C with LiCl in dimethylformamide. The spectra are taken from tetrahydrofuran (THF) solutions (1%) with THF as reference: (--) undegraded, (—) degraded 24 hr, (-·-) degraded 100 hr.

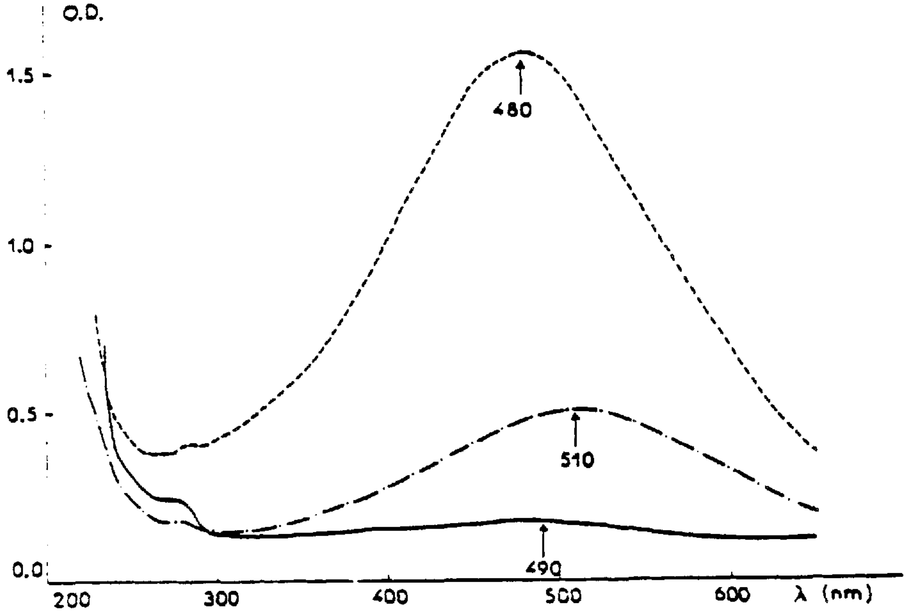


FIG. 6. UV-visible spectra of Copolymer D degraded at 50°C with LiCl in dimethylformamide. (—) degraded 3 hr. (-·-) degraded 6 hr. (--) degraded 24 hr. The spectra are taken from THF solutions [(—) 2%, (-·-) 1%, (--) 0.5%] with THF as reference.

in various conditions, a broad distribution of polyene sequences is formed. The shorter sequences, indicated by absorption at $\lambda < 300$ nm, are formed rapidly: possibly they come from initial selective dehydrobromination of VB diads and triads. As the process continues, longer sequences appear and become the dominant structures. This process is more rapid at higher temperature.

These features are observed also for Copolymer F with a higher bromine content. As shown in Fig. 7, short sequences appear more easily and are chiefly diads (243 nm) and triads (285 nm). When degradation increases the maximum of the optical density tends to be shifted to lower wavelengths, i.e., to shorter sequences. Most probably the dehydrohalogenation reaction is partly reversible and there is some random addition of HCl on the double bond in the long polyenes (Figs. 6 and 8). Finally, some data reported in Table 4 show that the degradation process also involves the breaking of a few chains, thus giving a fraction soluble in methanol which is more degraded than the whole polymer.

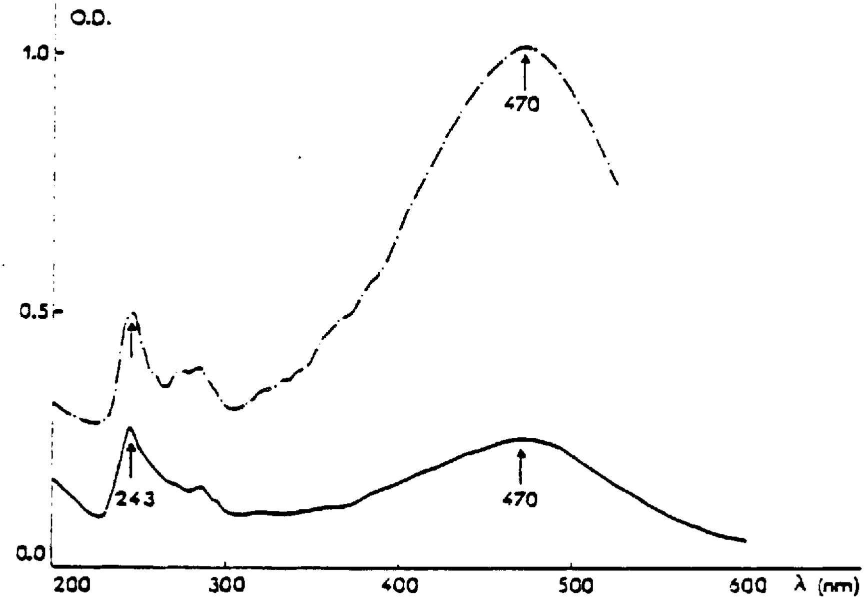
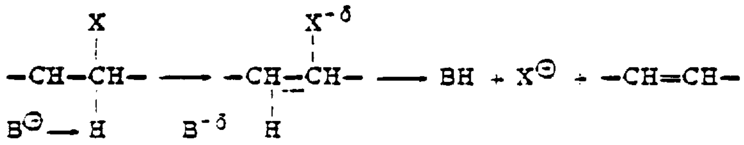


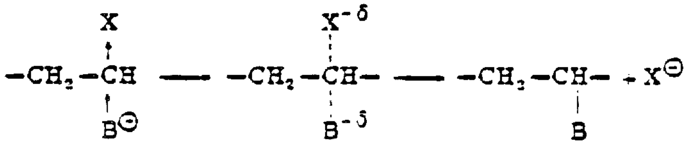
FIG. 7. UV-visible spectra of Copolymer F degraded at 30°C with LiCl in DMF during 24 hr (—) or 52 hr (---). The spectra are taken from 1% THF solutions with a solution of undegraded polymer as reference.

Dehydrobromination might be selectively produced only in the case of sequences of VB units. However, there is a tendency, as soon as these short polyene sequences are formed, for a chain elimination reaction leading to long sequences, and there is always competition between the elimination reaction and the substitution reaction. Possible mechanisms are for elimination E_2:



$$-CH-\overset{X}{\underset{B^{\ominus}\rightarrow H}{CH}}- \longrightarrow \underset{B^{-\delta}}{}-\underset{H}{CH}\!\overset{X^{-\delta}}{=\!CH}- \longrightarrow BH + X^{\ominus} + -CH{=}CH-$$

and for substitution:



$$-CH_2-\underset{\uparrow\atop B^{\ominus}}{\overset{X\atop\uparrow}{CH}} \longrightarrow -CH_2-\underset{B^{-\delta}}{\overset{X^{-\delta}}{CH}}- \longrightarrow -CH_2-\underset{B}{CH}- + X^{\ominus}$$

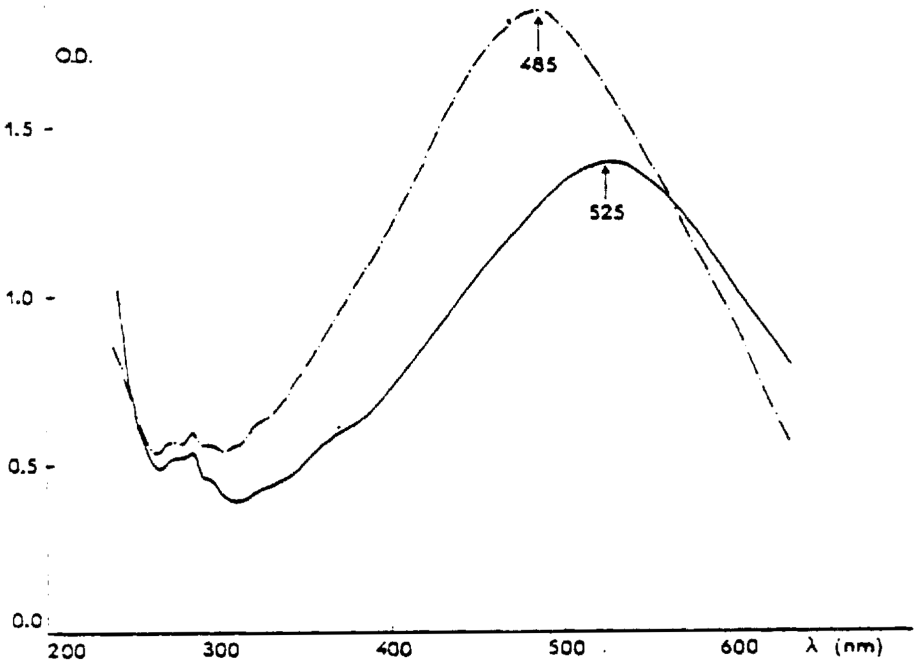
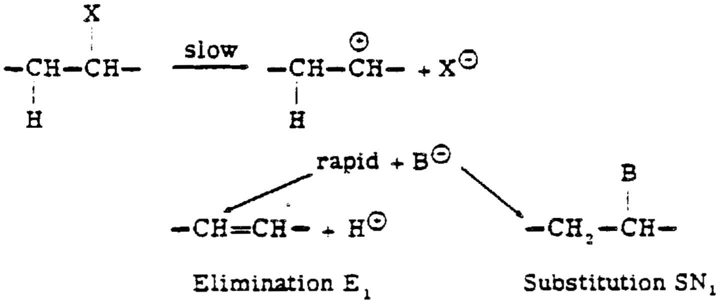


FIG. 8. UV-visible spectra of Copolymer F degraded at 50°C with LiCl in DMF during 3 hr (—) or 6 hr (--).

or



It seems that the elimination process is favored at higher temperatures while the substitution process is dominant at room temperature. Reversible addition of acids on double bonds and chain breaking are secondary processes.

In any event, ionic degradation fails to lead to the preparation of polymers with controlled distribution of internal short sequences of double bonds.

ACKNOWLEDGMENTS

The authors are indebted to Dr. J. Guillot for his help with the interpretation of copolymerization kinetics and the calculation of the sequence distribution, to Dr. M. Bert for experiments in thermal degradation, and to Miss G. Lhuillier for macromolecular weight measurements.

REFERENCES

[1] D. Braun and M. Thallmaier, J. Polym. Sci., Part C, 16, 2351 (1967).
[2] A. Michel, G. Schmidt, and A. Guyot, In Preparation.
[3] A. Guyot and J. Guillot, J. Chim. Phys., 61, 143 (1964).
[4] A. J. Devries, C. Bonnebat, and M. Carrega in IUPAC Macromolecular Chemistry—6, Butterworths, London, 1971, pp. 209-240.
[5] G. S. Park and D. G. Smith, Trans. Faraday Soc., 65, 1854 (1969).
[6] F. Danusso, G. Pajaro, and D. Sianese, Chim. Ind. (Milan), 41, 1170 (1959).
[7] A. Guyot and M. Bert, J. Appl. Polym. Sci., In Press.
[8] J. P. Roth, P. Rempp, and J. Parrod, J. Polym. Sci., Part C, 4, 1347 (1964).
[9] H. Gueniffrey and C. Pinazzi, C. R. Acad. Sci., Paris, 263, 915 (1966).

Accepted by editor January 8, 1973
Received for publication February 14, 1973