Studies of Free-Radical Alternating Copolymerization. IV. Quantitative Determination of the Influence of the Charge-Transfer Complex between the Comonomers on the Microstructure of Co(Vinyl Acetate-alt-(Citraconic Anhydride) Polymers

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ABSTRACT

Vinyl acetate and citraconic anhydride are known to give 1:1 radical alternating copolymers regardless of the monomer feed composition. The mechanism of this copolymerization involves free monomers and a charge-transfer complex between them. We undertook a study of the microstructure by NMR and thermogravimetric analysis (study of the thermal cis elimination of acetic acid). We determined a quantitative correlation between the theoretical proportion of D-A diads obtained in the reaction corresponding to the addition of the complex between comonomers on the growing chain and the microstructure of the copolymers determined by thermogravimetric analysis.

INTRODUCTION

Citraconic anhydride (3-methyl-2,5-furanedione, A) and vinyl acetate (D) give a complex (C) (charge-transfer complex). This formation is characterized by the following equilibrium:

$$A + D \rightleftharpoons C, \qquad K = [C]/([A] + [D]). \tag{1}$$
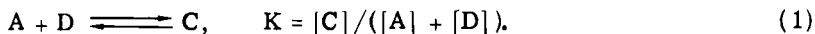
The equilibrium constant K is 0.52 L/mol at 300 K, and the ΔH of Reaction (1) is 5.7 kJ/mol [1]. Four propagation steps define the mechanism of the alternating copolymerization involving a charge-transfer complex between the monomers [1, 2]:

$$\sim\sim A^{\circ} + D \xrightarrow{\quad k_{AD} \quad} \sim\sim A\text{–}D^{\circ}, \tag{2}$$

$$\sim\sim A^{\circ} + C \xrightarrow{\quad k_{AC} \quad} \sim\sim D\text{–}A^{\circ}, \tag{3}$$

$$\sim\sim D^{\circ} + A \xrightarrow{\quad k_{DA} \quad} \sim\sim D\text{–}A^{\circ}, \tag{4}$$

$$\sim\sim D^{\circ} + C \xrightarrow{\quad k_{DC} \quad} \sim\sim A\text{–}D^{\circ}, \tag{5}$$
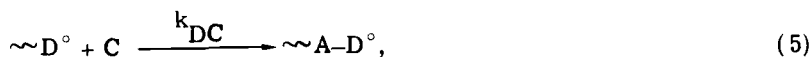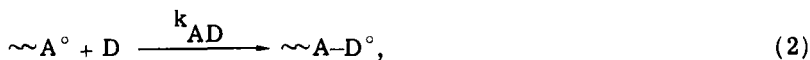
where $\sim\sim A^{\circ}$ and $\sim\sim D^{\circ}$ are growing chains terminated, respectively, by an A or a D unit. We have shown that $\beta_1 = k_{AC}/k_{AD} = 9.9$ and $\beta_2 = k_{DC}/k_{DA} = 3.6$ [1] in benzene (benzene does not complex citraconic anhydride). Starting from these values, it is possible to determine the probabilities $P(C/X)$ of adding the complex for a growing chain terminated by an X unit. These probabilities are given by Relations (6) and (7) [2c]:

$$P(C/A) = \beta_1 K [A]/(\beta_1 K [A] + 1), \tag{6}$$

$$P(C/D) = \beta_2 K [D]/(\beta_2 K [D] + 1). \tag{7}$$

The aim of this paper is to determine the influence of Reactions (3) and (5) on the microstructure of the alternating copolymers.

EXPERIMENTAL

Thermogravimetric analyses were done with a thermoanalyzer Setaram MTB 10^{-8} connected to an Apple II microcomputer with an Adalab interface (Interactive Microware Inc.) [3].

TABLE 1. Experimental Conditions for the Preparation of Alternating Copolymers

Polymer	1	2	3	4	5	6	7	8	9	10	11
[A], mol/L	0.115	0.12	0.165	0.27	0.40	0.42	0.50	0.54	0.69	0.87	1.6
M, mol/L	1.65	3	1.65	3	2	3	2	3	3	3	4

Infrared spectra of films were recorded with a Perkin-Elmer PE 680 instrument.

^{1}H NMR spectra of pyridine solutions containing TMS as internal standard were recorded with a Bruker WP 60 DS instrument. ^{13}C NMR spectra of the same solutions were recorded with a Bruker AM 400 WB instrument.

Polymerizations were conducted as described before [1] under the following conditions: [AIBN] 10 mmol/L, [A] + [D] = M, temperature 333 K, solvent: benzene. Table 1 gives the concentrations used in the preparation of the polymers.

RESULTS AND DISCUSSION

NMR Study

Figure 1 shows the ^{1}H NMR spectra of copolymers P4 and P10. Both copolymers exhibit the same resonances at 1.72, 2.14, 3.63, and 5.4 ppm. These resonances were assigned, respectively, to nuclei 4, 3 and 9, 1, and 5 (for nomenclature, see Fig. 1). Figure 2 shows the ^{13}C NMR spectra of polymers P4 and P10. Both copolymers exhibit the same resonances at 21, 22.6, 37.7, 47, 58.8, 68.6-75.4, 170.7, 173, and 178 ppm. These resonances were assigned, respectively, to nuclei 3, 9, 4, 5, 6, 1, 8, 2, and 7 (for nomenclature, see Fig. 2). In the case of poly(vinyl acetate), C1 and C4 are influenced by the stereoregularity of the polymer chain [4], and in some vinyl acetate copolymers C2 and C4 are sensitive to the distribution of the repeat units and to the tacticity [5]. Due to the poorly resolved spectra obtained, it is difficult to make a microstructure determination, but we conclude that all the copolymers studied have the same configuration (these polymers exhibit exactly the same ^{1}H and ^{13}C NMR spectra).

Thermogravimetric Study

Thermal degradation of maleic anhydride and vinyl acetate alternating copolymers shows (in the absence of oxygen) quan-
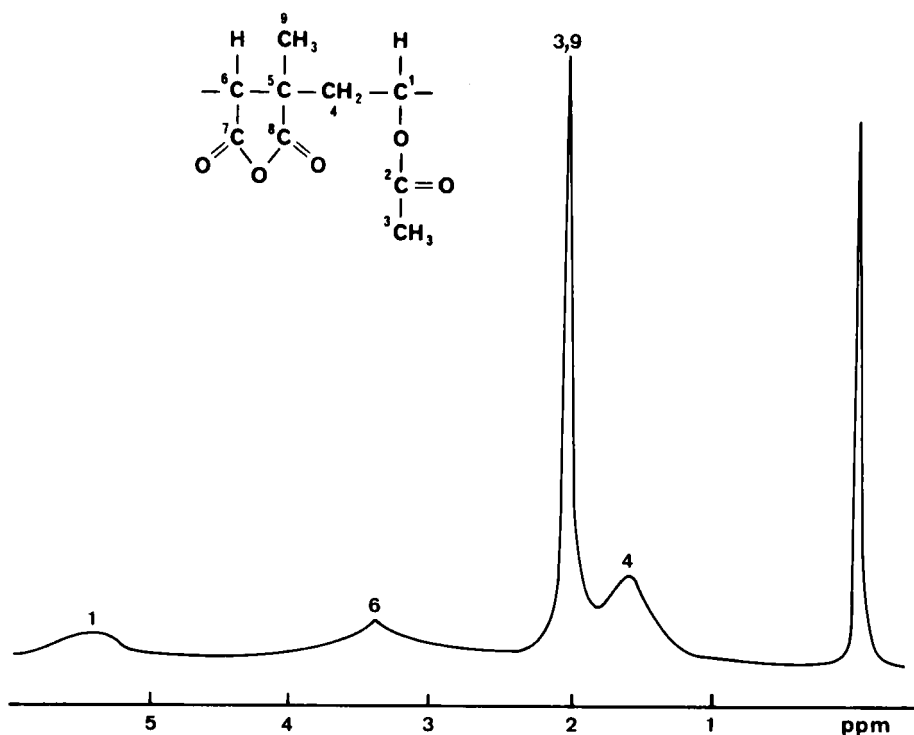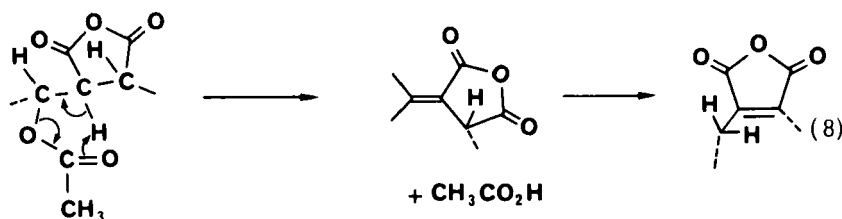
FIG. 1. ^{1}H NMR spectra of Polymers P4 and P10.

titative cis elimination of acetic acid through Reaction (8) [2c, 6]:

In the case of citraconic anhydride and vinyl acetate alternating co-
polymers, we observe the disappearance of the absorption of the ester
group at 1 745 cm^{-1} after heating at 180°C for 3 h under vacuum. This
disappearance corresponds to quantitative elimination of acetic acid
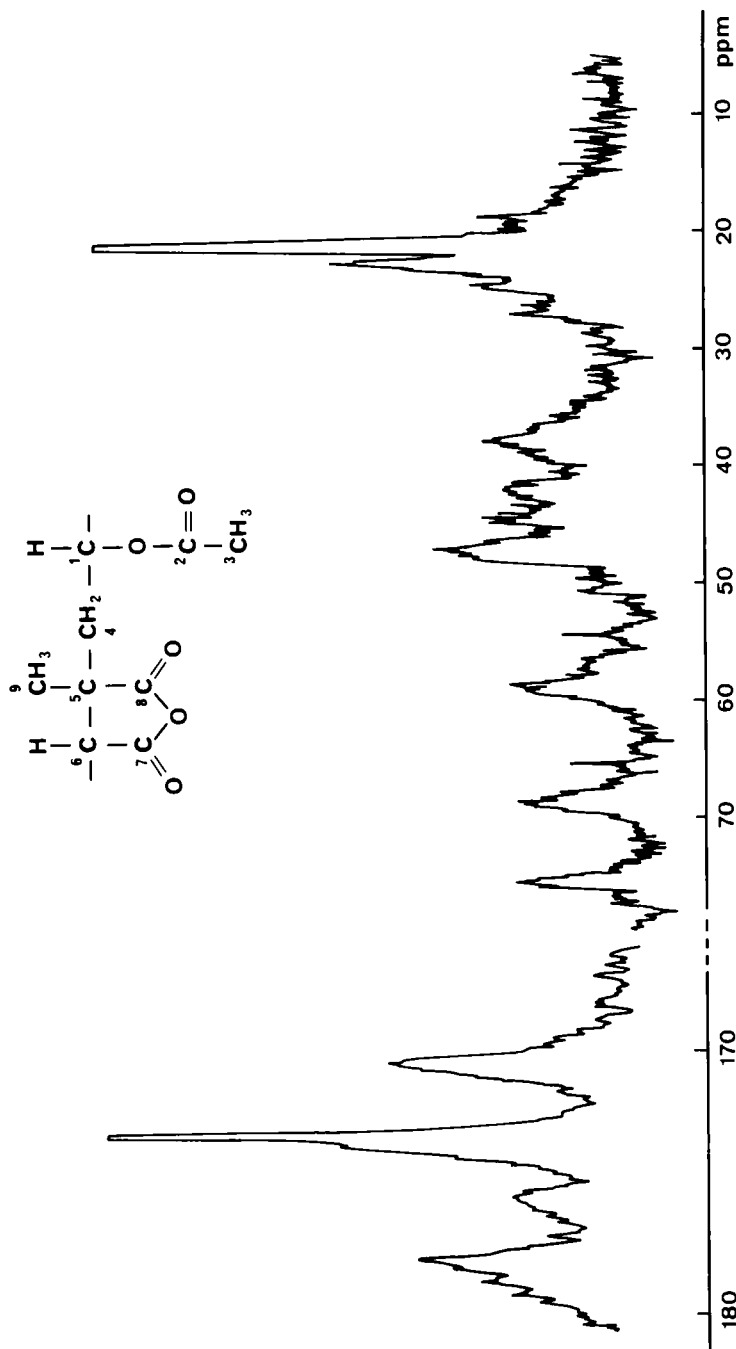and shows the isothermal decomposition of the copolymers reproduced

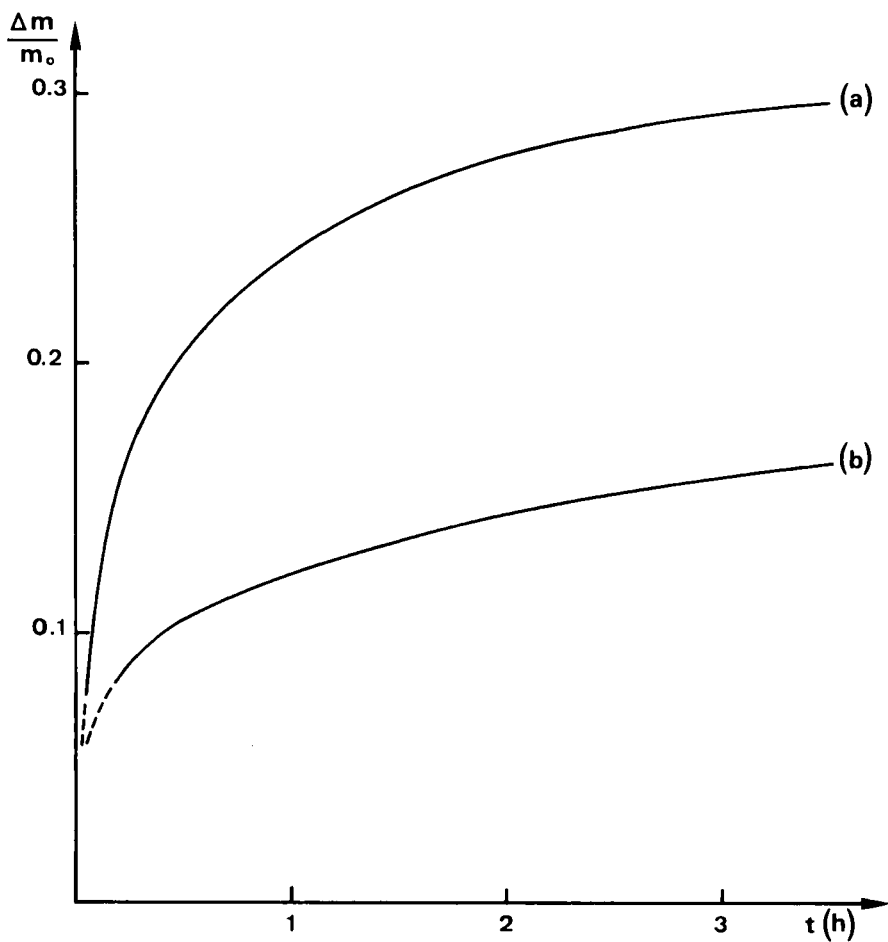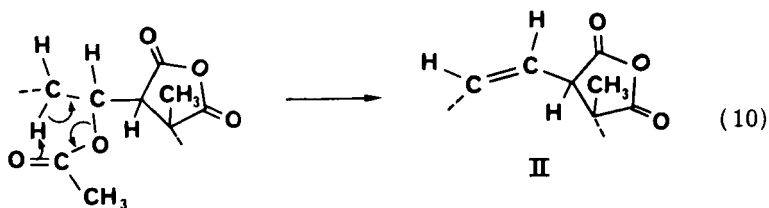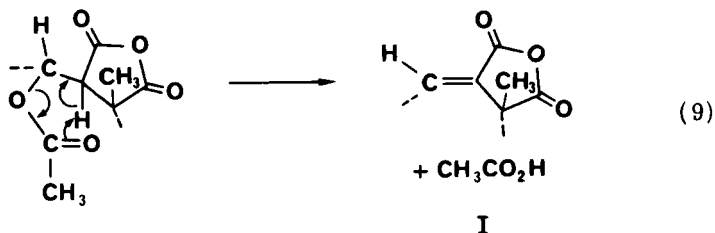FIG. 2. ^{13}C NMR spectra of Polymers P4 and P10.

FIG. 3. Isothermal decomposition of (a) Polymer P10 and (b) Polymer P5. $t = 180°C$; $\Delta m/m_0$ = relative weight loss on heating.

in Fig. 3. We have two possibilities of elimination of acetic acid, Reaction (9) or (10):

I   (9)

+ CH$_3$CO$_2$H

II   (10)

The distinction between Species I or II can be made by infrared spectrophotometry. The anhydride group exhibits two carbonyl absorption bands due, respectively, to the symmetric $\bar{\nu}_s$ and antisymmetric $\bar{\nu}_{as}$ vibration in the plane of the anhydride molecule. When there is a double bond conjugated to the carbonyl, we observe a lowering of the absorption bands by 20 to 40 cm^{-1} [1, 7]. This lowering is not observed for unconjugated double bonds. For all the alternating copolymers, we observe $1\,853 < \bar{\nu}_s < 1\,856$ cm^{-1} and $1\,782 < \bar{\nu}_{as} < 1\,787$ cm^{-1}, but after heating under vacuum at 180°C for 3 h, we obtain $1\,836 < \bar{\nu}_s < 1\,840$ cm^{-1} and $1\,773 < \bar{\nu}_{as} < 1\,779$ cm^{-1}. Thus, the double bond produced by the degradation is conjugated to the carbonyl group of the anhydride function and, therefore, the elimination of acetic acid is governed by Reaction (9).

The elimination is a first-order reaction, and the kinetics obey the relation

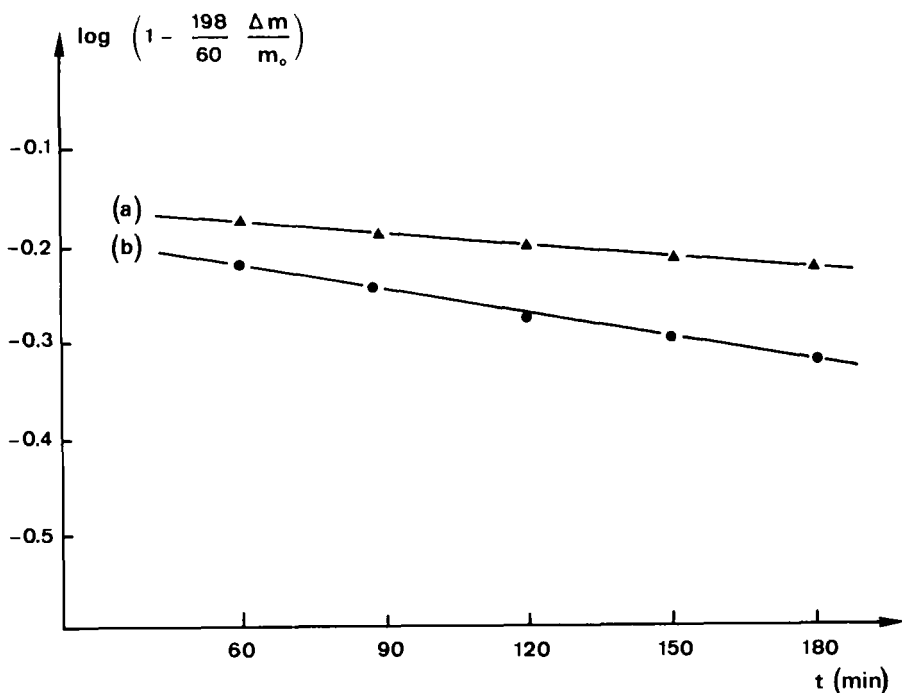$$\log\left(1 - \frac{198}{60}\,\frac{\Delta m}{m_0}\right) = -kt, \qquad (11)$$

$$\log \left(1 - \frac{198}{60} \frac{\Delta m}{m_o}\right)$$

FIG. 4. First-order kinetic plot of Reaction (9). Polymer 5. (a) T = 180°C. (b) T = 205°C.

where m_0 is the initial weight of the copolymer and Δm is the weight loss at time t (Fig. 4).

The TGA curves for Copolymers P2 and P10 in Fig. 5 show two different behaviors that can be explained by the existence of different stable conformers in different relative proportions. The transition state for the elimination reaction is apparent. In the threo configuration of the D-A diads, the transition state is obtained by hindered rotation around the C–O bond (angle χ) [8, 9]:
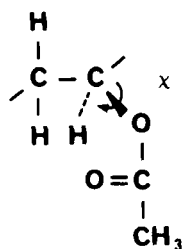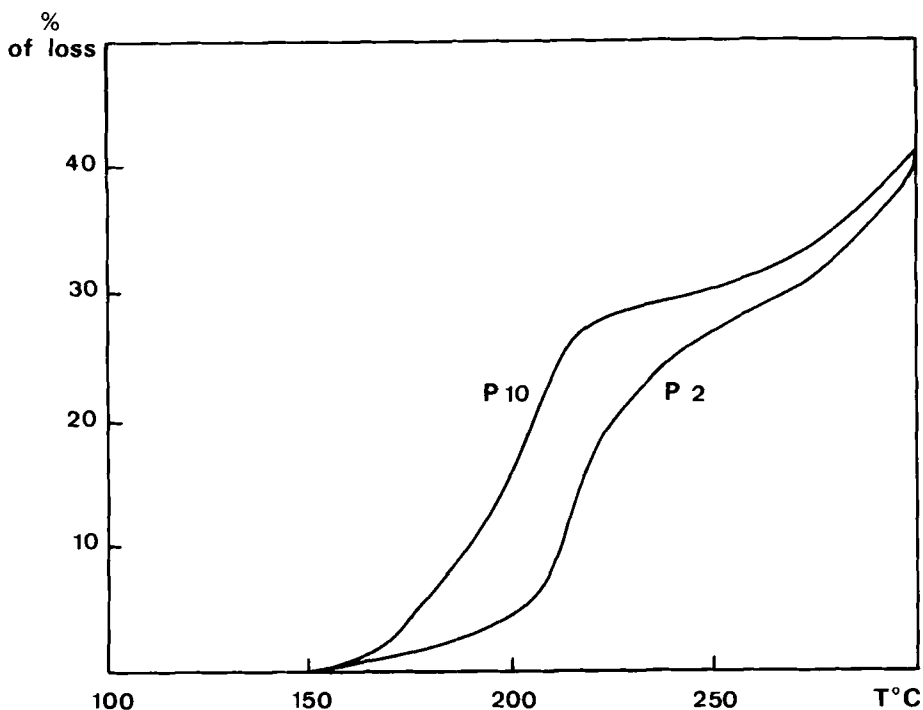
FIG. 5. TGA curves of Polymers P2 and P10.

All the different conformers have different activations energies. This assumption is in good agreement with the result obtained by isothermal degradation. In fact, if k_i is the rate constant of degradation of conformer i, α_i is the mole fraction of this conformer, and P is the molar concentration of D units, we can write

$$\frac{d[CH_3COOH]}{dt} = P \sum_{i=1}^{n} \alpha_i k_i = PK. \qquad (12)$$

Relation (11) is obtained by integration of Eq. (12).

The differential TGA curves of Polymers P1 to P11 (Fig. 6) indicate that the decomposition occurs in different states. The relative proportion of each decomposition depends on the relative concentration of monomer used in the polymer preparation. There are at least five steps of decomposition. We have determined the activa-
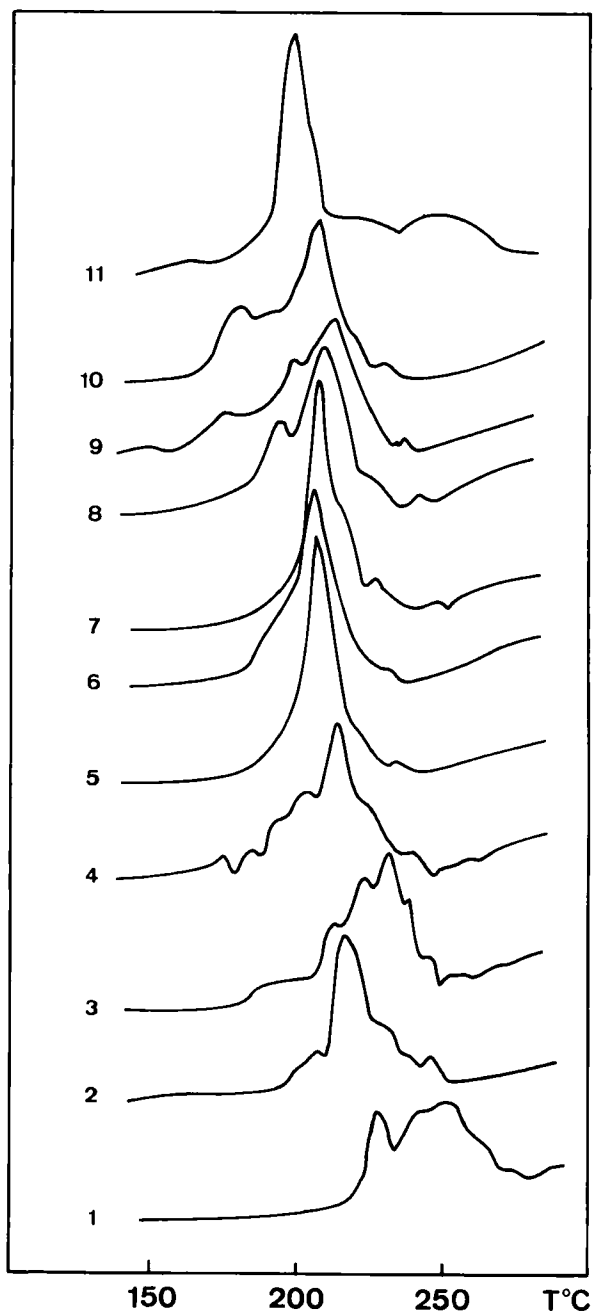
FIG. 6. DTGA curves of Polymers P1 to P11.

TABLE 2. Activation Energies of the First Three
Steps of the Degradation Reaction

Polymer	E_A, kJ/mol		
	Step 1	Step 2	Step 3
P2	113	190	-
P6	123	208	221
P8	126	174	225
P10	137	180	234

tion energy (E_A) of the three first steps by the method of Coats and
Redfern [10], assuming n = 1 (as seen in isothermal decomposition)
and varying the conversion from 0 to 1 for each step of decomposition
(Table 2).

D-A diads are obtained by Reaction (3) or (4). Appearance of De-
composition Steps 1, 2, and 3 is related to the probability of partici-
pation of the complex in Reaction (3) of propagation (variation of
probability P(C/A) is reported in Fig. 7). There is a linear relation
between the percentage of decomposition in the three steps and the
probability P(C/A), as shown in Fig. 8.
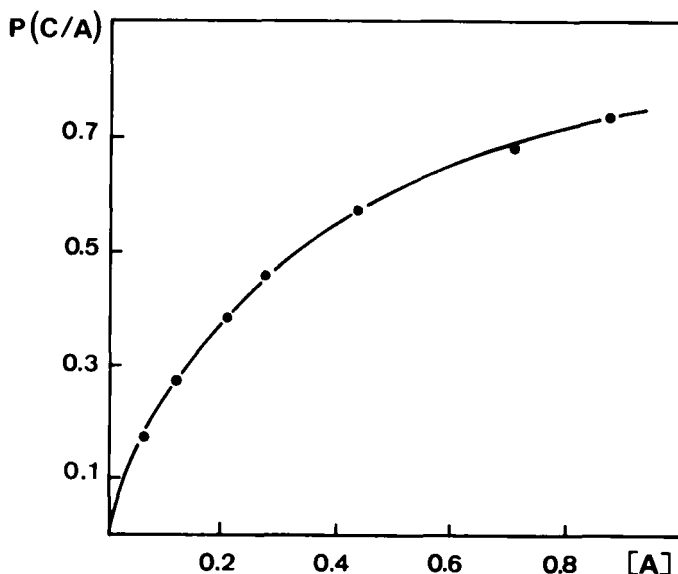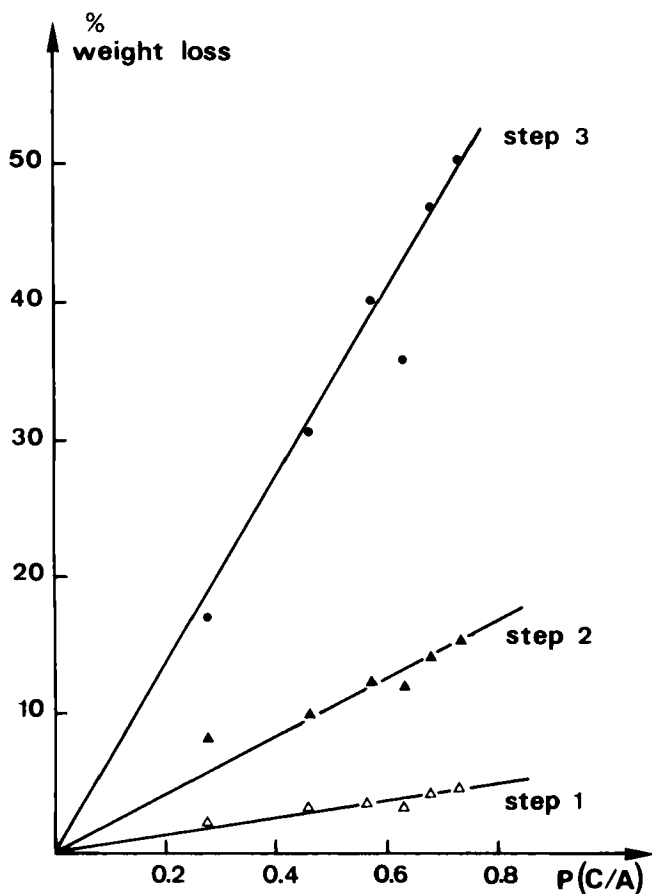

FIG. 7. Variation of the probability P(C/A) vs [A].

FIG. 8. Variation of the percentage of decomposition of Steps 1, 2, and 3 vs P(C/A).

CONCLUSION

NMR studies have shown that not all the copolymers exhibit signi-
ficant differences in their configuration independent of the experimental
conditions of the copolymerization (relative concentration of the mono-
mers). This result is in good agreement with literature results [1, 11].

Thermogravimetric analysis show different behaviors. As observed
for maleic anhydride-vinyl acetate alternating copolymers [2f], these
differences are due to differences in the conformation of the ester
group. When a growing chain adds a complex, two diads are formed;
for example, for Reaction (3) an A-D and a D-A diad. The A-D diad

has the same average configuration as the diad obtained by Reaction (2). The D-A diad is obtained by the addition of Monomer A of the complex to the growing chain. The transition state geometry is probably dependent on the conformation of the complex and induces a stereochemistry of the D-A diad different from that obtained by Reaction (4). This hypothesis is confirmed by the linear relation obtained between the percentages of decomposition by Steps 1, 2, and 3, characteristic of three differents conformations , and $P(C/A)$.

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