Studies of Radical Alternating Copolymerization. II. Influence of Charge Transfer Complex between Comonomers on the Microstructure of the Copolymers. Case of Maleic Anhydride and Vinyl Acetate

Claude Caze[a]; Claude Loucheux[a]

[a] Laboratoire de chimie macromoléculaire Université des Sciences et Techniques de Lille B.P., Villeneuve D'Ascq, France

PLEASE SCROLL DOWN FOR ARTICLE

Studies of Radical Alternating Copolymerization.
II. Influence of Charge Transfer Complex between Comonomers on the Microstructure of the Copolymers.
Case of Maleic Anhydride and Vinyl Acetate

CLAUDE CAZE and CLAUDE LOUCHEUX

Laboratoire de chimie macromoléculaire
Université des Sciences et Techniques de Lille
B.P. 36 59650 Villeneuve D'Ascq, France

ABSTRACT

Vinyl acetate and maleic anhydride are known to give 1:1
radical alternating copolymerization regardless of the monomer
feed composition. The mechanism of this copolymerization in-
volves free monomers and a complex between them (charge
transfer complex). We undertook a study of the microstructure
of different alternating copolymers (by ^{1}H, ^{13}C NMR, and thermo-
gravimetric analysis). Starting from the results obtained, we
determined the influence of the participation of the complex on
the microstructure of the alternating copolymers.

INTRODUCTION

Maleic anhydride (A) and vinyl acetate (D) give a complex (C)
(charge transfer complex) [1, 4]. This formation is characterized
by the equilibrium constant K defined by

$$A + D \rightleftharpoons C, \qquad K = [C]/[A][D] \qquad (1)$$

Three propagation steps define the mechanism of the alternating co-polymerization [1-3]:

$$\sim\sim D^\bullet + A \xrightarrow{\quad k_{DA} \quad} \sim A^\bullet \tag{2}$$

$$\sim\sim A^\bullet + D \xrightarrow{\quad k_{AD} \quad} \sim D^\bullet \tag{3}$$

$$\sim\sim A^\bullet + C \xrightarrow{\quad k_{AC} \quad} \sim A^\bullet \tag{4}$$

where $\sim A^\bullet$ and $\sim D^\bullet$ are growing chain terminated, respectively, by an A or D unit. When the copolymerization occurs in a solvent (S) which gives a complex (C_1) with maleic anhydride, a competition between Equilibriums (1) and (5) takes place. Then the concentration of the complex C decreases when K_1 increases.

$$S + A \rightleftharpoons C_1, \qquad K_1 = [C_1]/[S][A] \tag{5}$$
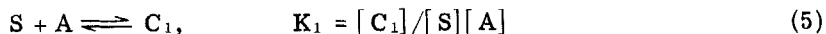
When the concentration of C becomes negligible, the mechanism of the copolymerization involves only Reactions (2) and (3) [1].

The conformation and the reactivity of the complex have been studied theoretically [3, 4]. The aim of this paper is to determine the influence of the participation of C on the microstructure of the alternating copolymers.

EXPERIMENTAL

Vinyl acetate was purified according to a procedure described in the literature [5]. Maleic anhydride was twice recrystallized from a purified chloroform solution, dried under reduced pressure, and then distilled under 10^{-1} torr pressure just before use. α,α'-Azoisobutyro-nitrile (AIBN) was recrystallized from ethyl alcohol and then dried under vacuum. All solvents were purified using standard procedures.

Polymerization

Pyrex polymerization vessels were charged with known quantities of freshly purified monomers, initiator, and solvent. After connection to a high vacuum line, their content was degassed, and then the vessels were sealed. The vessels were maintained during the time of polymerization in a thermostat adjusted at $\pm 0.1°C$. The polymerization was stopped at low conversion (maximum 10%) by a quick cooling of the polymerization vessel. The crude copolymers were precipitated in n-hexane and purified by successive dissolution in acetone and

TABLE 1. Experimental Conditions for the Synthesis of Copolymers
A and B

	A	B
Solvent	Benzene	Acetone
Temperature, $^\circ$C	60	70
Total concentration in comonomers (mole L^{-1})	2	2
Initial MA molar fraction	0.4	0.5
AIBN concentration (mole L^{-1})	5×10^{-3}	5×10^{-3}

precipitation in n-hexane. Then the copolymers were dried under
vacuum until constant weight is reached.

Microstructure Studies

The microstructure was studied by three methods: (1) ^{1}H NMR
(Cameca TSN 250 MHz), (2) ^{13}C NMR (Varian CFT 20), and (3) TGA
analysis under nitrogen (Adamel Type 2). NMR spectra were taken
from hexadeutered acetone solutions with TMS as internal standard.
IR spectra were recorded from films with a Perkin-Elmer 257
instrument.

RESULTS AND DISCUSSION

The microstructure studies were carried out on two alternating
Copolymers A and B. These two copolymers were synthesized in
the experimental conditions given in Table 1. In these conditions the
mechanism of the alternating copolymerization involves the participa-
tion of Reactions (2), (3) and (4) for Copolymer A and only Reactions
(2) and (3) in the case of Copolymer B [1].

^{13}C NMR

Figure 1 shows the spectra of Copolymers A (5×10^4 scans) and
B (10^5 scans). Both copolymers exhibit the same resonances at 173.1,
171.8, 171.5, 70.3-69.7, 51.6-50.4, and 41.6-40.6, about 34 and 21 ppm.
These resonances were assigned, respectively, to nuclei 2, 7, 8, 1, 6,
5, 4, and 3 (for nomenclature see Fig. 1). In the case of polyvinyl
acetate, Nuclei 1 and 4 are influenced by the stereoregularity of the
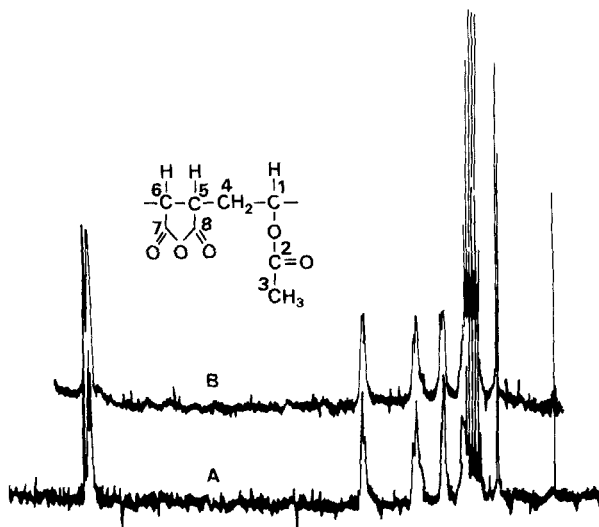polymer chain [6]. Our alternating copolymers exhibit for Carbon 1

FIG. 1. ^{13}C NMR spectra of Copolymers A and B (solution in hexadeuteroacetone, TMS as internal standard).

a doublet poorly resolved, and the resonance of Carbon 4 is perturbed by the peaks due to the solvent. Therefore the resonance of these two nuclei could not be used for the study of the microstructure. In the case of vinyl acetate copolymers [7], Carbons 2 and 4 of vinyl acetate units are sensitive to the distribution of repeat units along the copolymer and to the tacticity. Carbon 2 gives a singlet. This result confirms the alternating character of the copolymers, and it seems that the carbonyl of the ester group is always in the same surroundings. In consequence, the D-A diads to be always in the same configuration along the copolymer chain. Carbons 7 and 8 exhibit, respectively, a singlet. This result confirms the alternating character of the copolymers but does not give any information on the microstructure of the chain. The resonances of Carbons 5 and 6 are not sufficiently resolved for microstructure study.

^{13}C NMR shows that D-A diads from both Copolymers A and B exhibit the same configuration, and that these copolymers probably have the same microstructure.

^{1}H NMR

Figure 2 shows the spectra of Copolymers A and B. The two copolymers exhibit the same resonance at 2.1, 2.5, 3.5, and 5 ppm attributed, respectively, to Protons 1, 3, 4, and 2 (for nomenclature
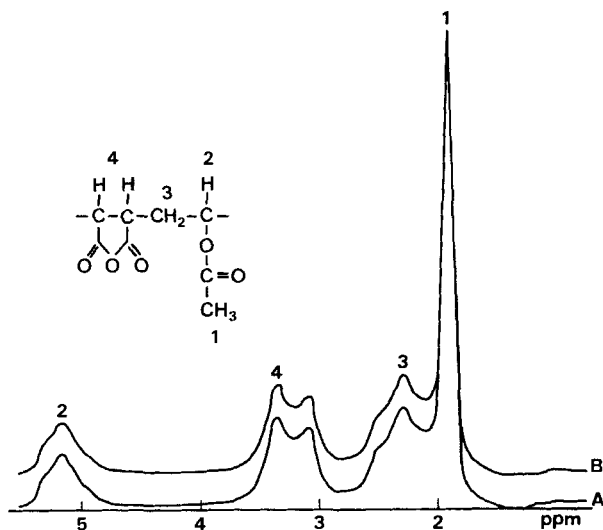
FIG. 2. ^{1}H NMR spectra of Copolymers A and B (solution in hexadeuteroacetone, TMS as internal standard).

see Fig. 2). These two spectra are poorly resolved and cannot be used for microstructure studies. Nevertheless, it seems that both copolymers do not show any large differences in their microstructures.

Thermogravimetric Analysis

Matsui and Aida [8] have studied the thermal degradation of alternating maleic anhydride/vinyl acetate copolymers. In the absence of oxygen we can observe a cis elimination of acetic acid through the reaction (6).

We first examined the possibility of Reaction (7) involving a methylenic proton of the polymer chain.

The distinction between Species I or II and III can be made by an infrared spectrophotometric study. The anhydride group exhibits two carbonyl absorption bands ν_S and ν_{AS} due, respectively, to the symmetric and antisymmetric carbonyl vibration in the plane of the anhydride molecule. When a double bond exists in Position 2 with regard to the carbonyl (conjugated double bond), we observe a lowering of the absorption frequency of 20 to 40 cm^{-1} [9]. This lowering is not observed in the case of an unconjugated double bond. Figure 3 shows the infrared spectra of a Copolymer A film before and after heating at 180°C for 10 hr. We point out the disappearance of the absorption due to the ester group and we observe a lowering of the ν_S and ν_{AS}
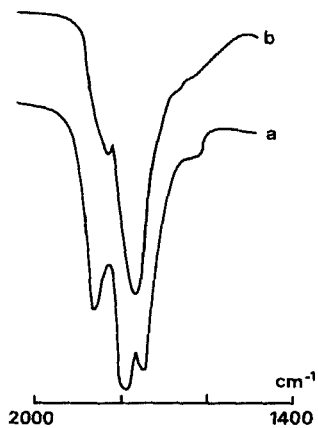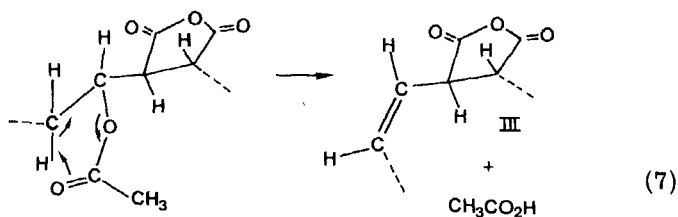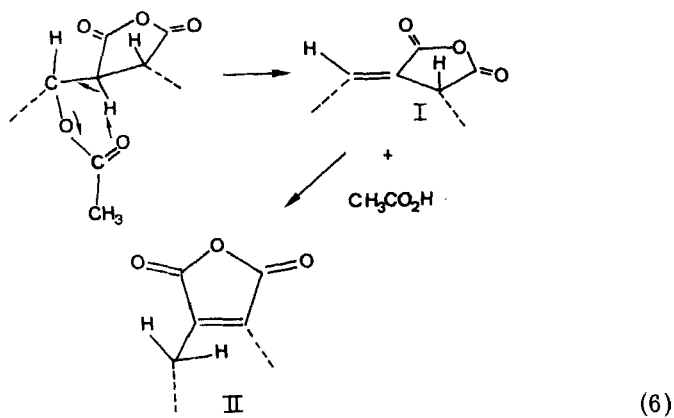
(6)

(7)

FIG 3. Variation of IR spectra of Copolymer A with (a) initial tem-
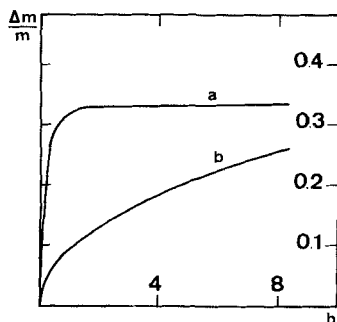perature and (b) after heating at 180°C for 10 hr.

FIG. 4. Isothermal decomposition of Copolymers A and B at 180°C.

carbonyl absorption bands 32 and 20 cm^{-1}, respectively. Thus the double bond produced by the degradation is conjugated to the carbonyl group of the anhydride function. The final state of elimination of acetic acid corresponds to Species I or II, therefore this elimination is governed by Reaction (6). This reaction is quantitative as shown in Fig. 4 which reports the weight loss vs time for Copolymer A at 180°C.

The ease of elimination is a function of the relative position of the ester group with regards to the α-proton support by the anhydride function. The reaction is only possible if the ester and the anhydride groups are in a threo configuration. This result confirms those obtained by ^{13}C NMR, in particular the single resonance peak of Carbon 2. The threo configuration of the D-A diads could be explained by steric hindrance due to the ester and anhydride groups in the copolymerization process.

The elimination is a first-order reaction and the kinetic obeys the relation

$$\log \left(1 - \frac{184}{60} \frac{\Delta m}{m_0}\right) = -kt \tag{8}$$

where m_0 is the initial weight of the copolymer and Δm is the weight loss at time t. Figure 4 compares the isothermal decomposition of Copolymers A and B at 180°C. Figure 5 shows the linear determination of constant k according to Relation (8). The values of K are reported in Table 2. At the same temperature, these values are quite different for both copolymers. A tentative explanation can be given. The transition state for these eliminations is plain. In the threo configuration, D-A diads of Copolymers A and B must have different stable conformations. That NMR spectra are poorly resolved for these different stable conformations are not detected from our NMR study.
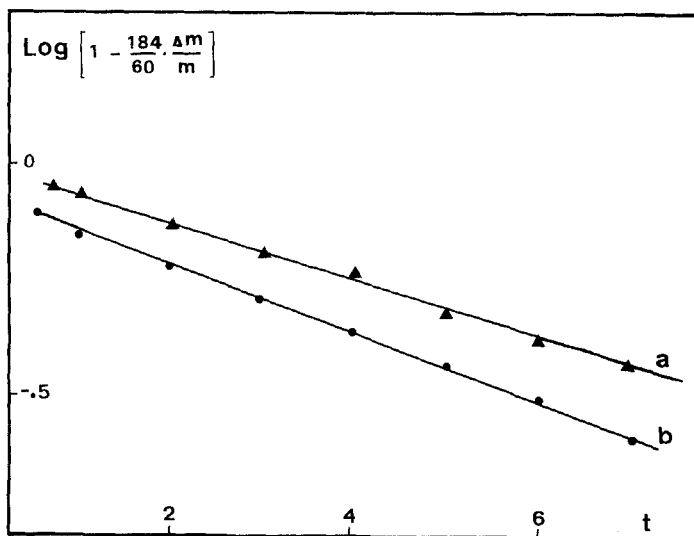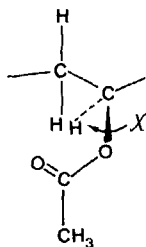
$$\text{Log}\left[1 - \frac{184}{60} \cdot \frac{\Delta m}{m}\right]$$

FIG. 5. Linear determination of k according to Relation (8): (a) Copolymer A at $160°C$; (b) Copolymer B at $180°C$.

TABLE 2. K Values (in sec^{-1}) for Copolymers A and B at 160 and $180°C$

Copolymer	t (°C)	
	160	180
A	3.8×10^{-5}	2×10^{-3}
B	3×10^{-6}	4.5×10^{-5}

Actually the polymeric chains bearing acetate lateral groups show a rotation hindrance around the —C—O— bond (angle X) [10, 11].
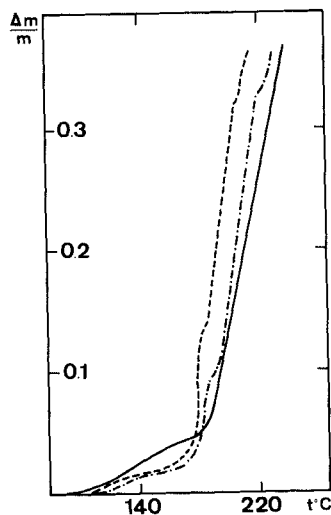
FIG. 6. Thermogravimetric analysis of the decomposition of Copolymer B at three heating rates: (- -) 4°C/hr, (- ·) 24°C/hr, and (—) 80°C/hr.

This hindrance can explain the existence of different stable conformers.

We made a programmed thermogravimetric analysis of Copolymers A and B at various heating rates. Figure 6 shows the weight loss of Copolymer B vs temperature at three heating rates: 4, 24, and 80°C/hr. At a heating rate of 24°C/hr, four successive steps of degradation appear in the temperature ranges 110-165, 165-178, 178-185 and 185-215°C. Figure 7 compares the weight loss of Copolymers A and B at a heating rate of 24°C/hr. The same ranges of degradation are obtained but the relative importance of each degradation step is different, as shown in Table 3. This result can be explained by the existence of different stable conformers as assumed above. These different conformers exist in the two copolymers but in different proportions. 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 the first conformer α_i is the molar fraction of this first conformer, and P is the molar concentration of D units, we can write

$$\frac{d[CH_3COOH]}{dt} = \sum_{i=1}^{n} \alpha_i Pk_i = P \sum_{i=1}^{n} \alpha_i k_i = Pk \qquad (9)$$

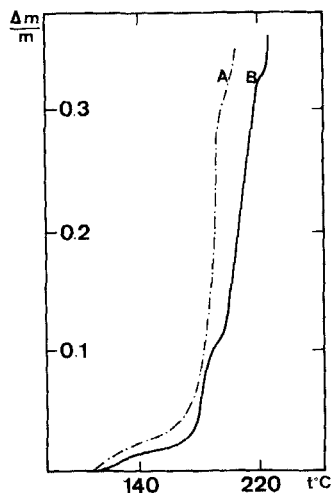By integration of Eq. (9), Relation (8) is derived.

FIG. 7. Comparison of the decomposition of Copolymers A and B at 24°C/hr.

TABLE 3. Relative Importance of Each Degradation Step for Copolymers A and B (heating rate: 24°C/hr)

t (°C)	110-165	165-178	178-185	185-215
A	12.2%	12.2%	64.4%	11.2%
B	6.1%	4.6%	16.9%	72.4%

We can relate the differences observed in the conformation of Copolymers A and B to the mechanism of copolymerization. D-A diads are obtained by Reaction (2) or (4). In Reaction (4) we have the addition of the two monomeric molecules of the complex on the growing chain, so the geometry of the transition state must be governed by the conformation of the complex. In consequence, D-A diads obtained by Reaction (4) should have a different conformation from the D-A diads obtained by Reaction (2).

CONCLUSIONS

NMR studies have shown that Copolymers A and B do not exhibit any significant difference in their configurations. This result is in good agreement with the one obtained by Bacskai et al. [12]. These

authors have shown that some alternating isobutene/maleic anhydride copolymers have the same configuration independent of the experimental conditions of the copolymerization (solvent, temperature, concentration).

Thermogravimetric analysis shows different behaviors. We made the hypothesis that this is due to differences in the conformation of the ester group. Starting from this hypothesis we proposed an explanation generalizable in all radical copolymerization involving a complex between the comonomers in the propagation steps. When a growing chain adds a complex, two diads are formed. For example, in the case of Reaction (4), an A-D and a D-A diad. The A-D diad has the same average configuration as the diad obtained by Reaction (3). The D-A diad is obtained by the addition of Molecule A of the complex on the growing chain. Then 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 (2).

REFERENCES

[1] C. Caze and C. Loucheux, J. Macromol. Sci.–Chem., A9, 29 (1975).
[2] G. S. Georgiev and V. P. Zubov, Eur. Polym. J., 14, 93 (1978).
[3] R. Arnaud, C. Caze, and J. Fossey, J. Macromol. Sci.–Chem., A14, 1269 (1980).
[4] D. Ghesquiere, R. Arnaud, and C. Caze, J. Phys. Chem., 83, 2029 (1979).
[5] S. I. Nozakura, Y. Morishima, and S. Murahashi, J. Polym. Sci., Polym. Chem. Ed., 10, 2853 (1972).
[6] Y. Inoue, R. Chujo, A. Nishioka, S. Nozakura, and H. Limuro, Polym. J., 4, 244 (1975).
[7] T. Kainu, D. W. Ovenall, and G. Reddy, J. Polym. Sci., Polym. Chem. Ed., 12, 901 (1974).
[8] S. Matsui and H. Aida, Chem. High Polym. Jpn., 26, 10 (1969).
[9] Monographies de chimie organique, Vol. 9, Masson, Paris, 1974, p. 129.
[10] P. R. Sudararajan, Macromolecules, 11, 256 (1978).
[11] Sarko and Marchessault, J. Am. Chem. Soc., 89, 6454 (1967).
[12] R. Bacskai, L. P. Lindeman, and D. L. Rabenstein, J. Polym. Sci., Polym. Chem. Ed., 10, 1297 (1972).