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C. Pichot[a]; J. Guillot[a]; A. Guyot[a]
[a] Laboratoire de Cinétique Chimique Macromoléculaire, Université "Claude Bernard", Villeurbanne, France

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Acid-Catalyzed Methanolysis of Vinyl Acetate Polymers and Copolymers. II.
Vinyl Chloride-Vinyl Acetate Copolymers

C. PICHOT, J. GUILLOT, and A. GUYOT

Laboratoire de Cinétique Chimique Macromoléculaire
Université "Claude Bernard"
Villeurbanne, France

ABSTRACT

Acid (HCl) catalyzed methanolysis of vinyl acetate-vinyl chloride copolymers was carried out in solvent mixtures with various amounts of methanol and tetrahydrofuran. The effect of the solvent composition on the initial rate suggests the existence of preferential solvation. The initial rate may be explained in terms of sequence distribution. The acceleration noted in polyvinyl acetate homopolymers disappears as soon as the vinyl chloride content is higher than 30%.

INTRODUCTION

A kinetic study of the acid-catalyzed methanolysis of polyvinyl acetate, reported in the first paper of this series [1], showed that the uncorrected initial rate was first order vs methanol concentration in solvent mixtures of methanol and tetrahydrofuran (THF), while the degree of acceleration decreased with increasing THF concentration.

A correction is to be applied to take into account the dissociation of the acid catalyst (HCl) which changes with the solvent composition. This correction is large, but it is difficult to estimate it with accuracy.

With this as background, the purpose of the present paper is to try to correlate the kinetic parameters of the acid-catalyzed methanolysis of vinyl chloride (C)-vinyl acetate (A) copolymers with the sequence distribution. Such a correlation between the sequence distribution and the chemical reactivity in a copolymer has been well established in other cases [2]. Arranz et al [3] have studied the base-catalyzed hydrolysis of vinylic esters copolymers and noted the stabilizing effect of steric hindrance. More recently, Nicolaev et al. [4] studied the acid-catalyzed (SO_4H_2) methanolysis of styrene-vinyl acetate copolymers and concluded that the initial rate was not dependent on the copolymer composition, while the acceleration degree increases with the vinyl acetate content. A detailed kinetic study of C-A copolymerization has been published [5], and the sequence distribution may be accurately calculated from it. An anomalous kinetic behavior has been noted which was later interpreted [6] in terms of an internal transfer reaction leading to the formation of short branches. Their possible influence on the methanolysis rate will also be examined in the present paper.

The experiments have been made using copolymers prepared either in suspension [6] or in solution [5], and the methanolysis was carried out as previously described [1].

RESULTS AND DISCUSSION

Most of the results are reported in Table 1 for either solution or suspension copolymers with different solvent mixtures of THF and methanol. Runs 1 and 2 recall previous results [1] concerning polyvinyl acetate homopolymers. Runs 3 to 22 correspond to suspension polymerization; Runs 23 to 27 to solution copolymerization which leads to lower molecular weights. The values of the limiting viscosity numbers η have been measured at 25°C in the solvent mixture considered. $\overline{M}_n$ has been obtained from membrane or vapor pressure osmometry. Runs 6-9 allow one to check that, the reaction is first order vs HCl concentration by considering the uncorrected values of the initial rate k_0. Of course, the true $\{H^+\}$ concentration is lower, particularly when the THF concentration is high. A correction was made which leads to a large increase in k_0 values; comparison of Runs 6-8 with run 9 indicates that the correction is probably not very accurate. The uncorrected values reported in Table 1 have been obtained by assuming that, for any copolymer,

$$-\frac{d\{A\}}{dt} = k_0\{A\}\{HCl\}\{CH_3OH\}$$

The corresponding corrected values were obtained by replacing $\{HCl\}$ with $\{H^+\}$ in the above equation, using the method previously described to calculate $\{H^+\}$.

Runs 11-16 illustrate the results for the same copolymer in different solvent mixtures. The low value for Run 11 is certainly due to the insolubility of the copolymer in the solvent. When the solubility is good enough (Runs 13 and 14) the reproducibility is quite good and the value of k_0 is not sensitive to small variations of $\{A\}$ or $\{HCl\}$. In the range of good solubility the k_0 value decreases with increasing THF contents. This trend is general for all the copolymers as shown in Table 2 where a comparison is made for two solvent mixtures with 60 and 81% THF, respectively. It is also valid for the corrected values and where the ratio of k_0 for the two solvent mixtures is not too greatly dependent on the copolymer composition. The situation is not the same for the homopolymer where the reverse is true (after correction). In the latter case the increase of the k_0 value with increasing THF content has been attributed to a chain expansion effect which causes a better accessibility of CH_3OH. The expansion of the copolymers (as measured by the ratio of the limiting viscosity numbers) is about the same as that of the homopolymer. However, the accessibility of the acetate groups to attack by CH_3OH may be more limited because of a preferential solvation of the copolymers by THF.

It appears that the initial rate constant k_0 in the same solvent mixture is dependent on the copolymer composition. This point is illustrated in Fig. 1 where the uncorrected values are plotted for three series of experiments: suspension copolymers and solution copolyers in a solvent mixture with 60% THF, and suspension copolymers in a solvent mixture with 81% THF. It is clearly seen that there is no large difference between suspension and solution copolymers; therefore the molecular weight is not an important parameter for the initial methanolysis rate. The same is true for short branching of the copolymer caused by an internal transfer reaction and which, owing to a competitive effect between propagation and transfer, is more important in solution polymerization.

In order to see if the maximum of k_0, which appears for each series of experiments, might be interpreted in terms of sequence distribution, a limited study of the methanolysis of model compounds has been carried out. The chosen models were 2,4-diacetopentane, 2,4,6-triacetoheptane, and 2-aceto-4-chloropentane, prepared according to the literature [7]. The different values for k_0 are reported in Table 3. This shows that an adjacent unit of vinyl chloride may be expected to

TABLE 1. Results of Methanolysis

Run	A (mole %)	C (mole %)	η (CGS)	$\overline{M}_n$	THF (mole %)	CH_3OH (mole %)	HCl mole %	A mole %	-dA/dt mole/liter $\times 10^3$	$k_0 \times 10^3$	$k_0 \times 10^3$, corrected	m
1	100	0	345		60	40	0.156	0.093	0.055	0.169	1.69	18
2	100	0	374		81	19	0.645	0.140	0.0240	0.107	3.10	6
3	70	30	66.2	109,500	60	40	0.400	0.072	0.070	0.392	3.92	10
4	70	30	71.8		81	19	0.645	0.110	0.023	0.131	3.90	0.5
5	63	37			60	40	0.355	0.066	0.082	0.56	5.64	1.5
6	47	53	95.8	67,200	60	40	0.568	0.051	0.123	0.68	6.84	0.8
7	47	53			60	40	0.290	0.051	0.064	0.70	6.98	-
8	47	53			60	40	0.145	0.051	0.030	0.65	6.20	-
9	47	53			60	40	0.070	0.051	0.014	0.65	4.7	-
10	47	53	100.3		81	19	0.536	0.080	0.020	0.18	5.2	-
11	30	70	gel		32	68	0.25	0.043		0.176	0.176	-
12	30	70	64.0		50	50	0.214	0.043		0.520	-	0.5
13	30	70	62.0	47,700	60	40	0.193	0.035	0.065	0.70	7.0	0
14	30	70	62.0		60	40	0.25	0.043		0.68	6.8	0
15	30	70	69.0		71	29	0.25	0.043		0.31	5.6	0
16	30	70	68.0		81	19	0.258	0.053	0.0068	0.20	5.2	0
17	22	78	63.2	36,000	60	40	0.160	0.027	0.040	0.58	5.3	0
18	22	78	72.3		81	19	0.430	0.053	0.0065	0.18	4.8	0
19	13	87	74.2	52,500	60	40	0.090	0.016	0.011	0.49	4.0	0
20	13	87	90.0		81	19	0.129	0.044	0.0022	0.15	3.1	0
21	5	95	86.5		60	40	0.107	0.010	0.0036	0.52	4.2	0
22	5	95	98.1		81	19	0.215	0.012	0.0009	0.136	2.9	0
23	68	32			60	40	0.377	0.056	0.074	0.50	5.0	3
24	46	54			60	40	0.345	0.057	0.080	0.56	5.6	1
25	29	71			60	40	0.166	0.027	0.021	0.70	7.0	0
26	19	81		2,600	60	40	0.365	0.040	0.045	0.49	4.9	0
27	10	90			60	40	0.182	0.023	0.011	0.45	4.5	0

TABLE 2. Influence of the Composition of the Solvent Mixture

Run	1, 2	3, 4	6, 10	13, 16	17, 18	19, 20	21, 22
A, mole %	100	70	47	30	22	13	5
V, mole %	0	30	53	70	78	87	95
$\frac{k_0\,(60\%\ \mathrm{THF})}{k_0\,(81\%\ \mathrm{THF})}$, uncorrected	1.58	3.0	3.8	3.50	3.20	3.30	3.80
corrected	0.54	1.00	1.32	1.34	1.10	1.31	1.45
$\frac{\eta\,(60\%\ \mathrm{THF})}{\eta\,(81\%\ \mathrm{THF})}$	0.92	0.92	0.95	0.91	0.88	0.82	0.88
$\frac{m\,(60\%\ \mathrm{THF})}{m\,(19\%\ \mathrm{THF})}$	3.0	20	-	-	-	-	-

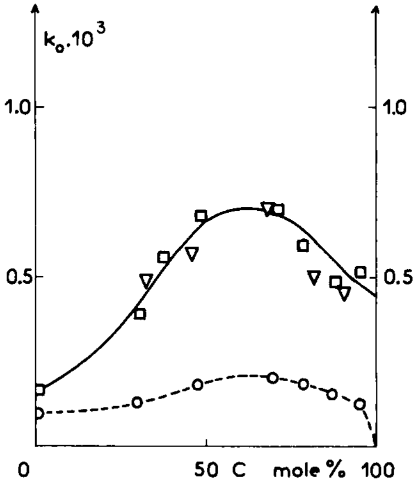

FIG. 1. Uncorrected values of the initial rate constant vs copolymer composition. Solvent mixture: 60% THF (——) suspension (□) and solution (▽) copolymer, and 81% THF (--) suspension (○) copolymers.

cause a better inductive accelerating effect on the methanolysis rate of the acetate group than one or two adjacent units of vinyl acetate.

We first tried to interpret the variation of k_0 in terms of triads by considering a central A unit with two adjacent units being either two A units, or one A and one C, or two C units. If α, β, and γ are the proportions of A units centered in these three kinds of triads, and k_{AAA}, k_{AAC}, and k_{CAC} are the respective initial rate constants, then the overall rate constant may be expressed as

$$k_0 = \alpha k_{AAA} + \beta k_{AAC} + \gamma k_{CAC}$$

The proportions α, β, and γ are plotted vs copolymer composition in Fig. 2. They have been calculated from the sequence distribution of the copolymer with known reactivity ratios [5] $r_A = 0.29$ and $r_C = 1.65$.

k_{AAA} is known from Run 1. Its value is 0.169×10^{-3} for a 60% THF mixture. For k_{CAC}, it is convenient to consider the extrapolated value of the curve of Fig. 1. We have chosen 0.45×10^{-3}. From the known values of α, β, and γ and the experimental values of k_0 for each copolymer, it was then possible to calculate k_{CAA}. The calculated

TABLE 3. Methanolysis of Model Compounds

Acetate model	HCl (moles/liter)	$\frac{\text{THF}}{\text{THF + MeOH}}$ (mole %)	$k_0 \times 10^3$	$k_0 \times 10^3$, corrected
Diethylcarbinol	0.160	60	0.78	7.8
Diacetopentane	0.182	60	0.97	9.7
Triacetoheptane	0.182	60	1.20	12.0
2-Aceto-4-chloropentane	0.182	60	1.60	16.0
Polyvinyl	0.160	60	0.169	1.69

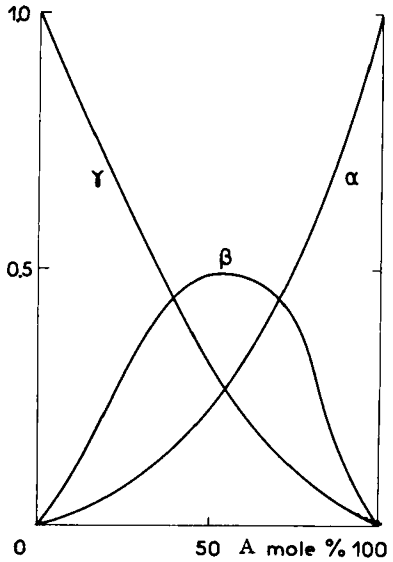

FIG. 2. Proportion α, β, and γ of triads AAA, AAC, and CAC as a function of the copolymer composition.

TABLE 4. Calculated Values of k_{CAA} for Methanolysis in a Solvent Mixture with 60% THF, Assuming $k_{AAA} = 0.169$ and $k_{CAC} = 0.45$

Run	A (mole %)	C (mole %)	α	β	γ	$k_0 \times 10^3$, experimental	$k_{CAA} \times 10^3$
1	100	0	1	0	0	0.169	-
3	70	30	0.46	0.43	0.10	0.390	0.60
5	63	37	0.40	0.47	0.13	0.560	0.90
6	47	53	0.19	0.50	0.31	0.680	1.01
13	30	70	0.04	0.34	0.63	0.700	1.20
17	22	78	0.02	0.25	0.72	0.58	1.02
19	13	87	0.002	0.09	0.908	0.49	0.94
21	5	95	0.001	0.05	0.95	0.52	2.88
23	68	32	0.43	0.46	0.11	0.49	0.80
24	46	54	0.15	0.47	0.37	0.56	0.78
25	29	71	0.05	0.34	0.61	0.70	1.22
26	19	81	0.02	0.22	0.76	0.50	0.72
27	10	90	0.004	0.11	0.88	0.45	0.49

TABLE 5. Calculated Values of k_{CAA} for Methanolysis in a Solvent Mixture with 81% THF, Assuming $k_{AAA} = 0.107$ and $k_{CAC} = 0.136$

Run	A (mole %)	C (mole %)	α	β	γ	$k_0 \times 10^3$	$k_{CAA} \times 10^3$
2	100	0	1.0	0	0	0.107	-
4	70	30	0.46	0.43	0.11	0.131	0.157
10	47	53	0.19	0.50	0.31	0.181	0.235
16	30	70	0.04	0.34	0.63	0.200	0.323
18	22	78	0.02	0.22	0.72	0.180	0.362
20	13	87	0.002	0.09	0.90	0.150	0.306
22	5	95	0.001	0.05	0.95	0.136	0.163

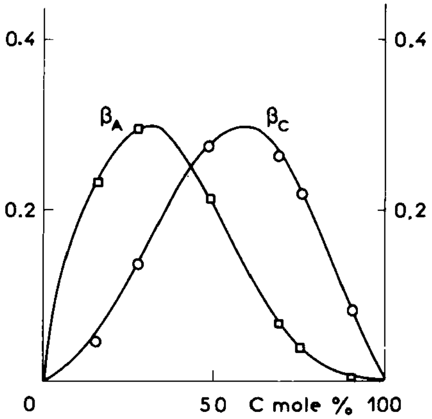

FIG. 3. Partial proportion β_A and β_C of tetrads CAAA and CAAC among the triads CAA.

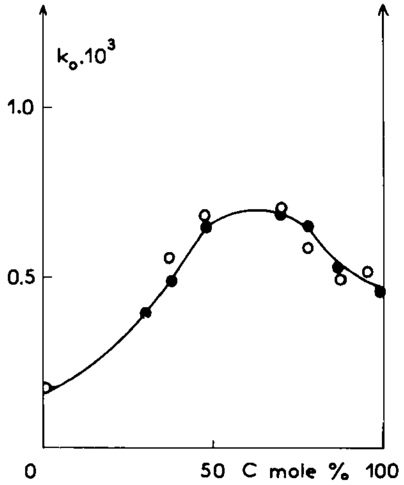

FIG. 4. Calculated (●) and experimental (○) uncorrected values of k_0 for a solvent mixture with 60% THF taking into account the tetrads.

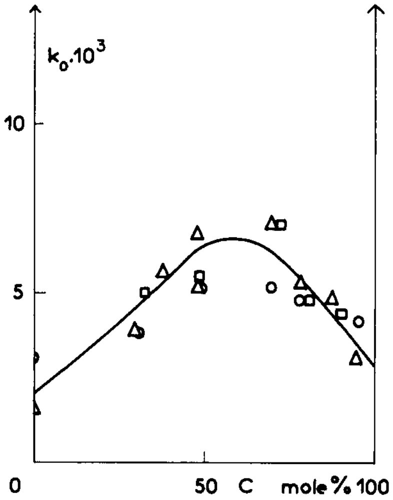

FIG. 5. Calculated (——) and experimental [(○) suspension 81% THF, (△) suspension 60% THF, (□) solution 60% THF) corrected values of k_0 assuming $k_{AAA} = 2 \times 10^{-3}$, $k_{CAC} = 3 \times 10^{-3}$, $k_{CAAA} = 4 \times 10^{-3}$, and $k_{CAAC} = 15 \times 10^{-3}$.

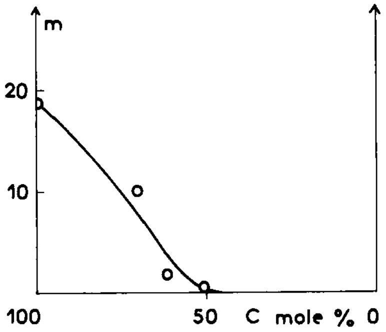

FIG. 6. Acceleration degree m vs copolymer composition.

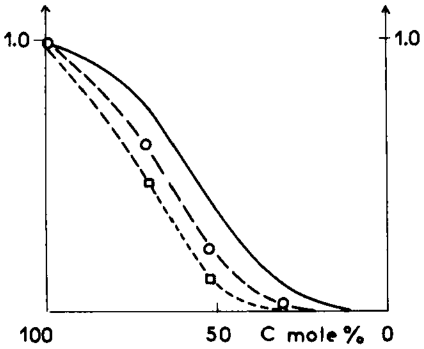

FIG. 7. Fraction of A units in sequences longer than 3 (——), 4 (— —) or 5 (--) units.

values are reported in Table 4. It may be seen that k_{CAA} is not constant but goes through a maximum. The same conclusion is true for the solution copolymers in the same solvent mixture, as well as for the suspension copolymers in a 81% THF solvent mixture (Table 5).

However, it may be convenient to distinguish among the CAA triads those belonging to tetrads CAAA and CAAC, respectively. The later are expected to have an increased reactivity owing to the influence of two C units. Tables 4 and 5 show that the maximum value of k_{CAA} corresponds to the same copolymer composition (30% A, 70% C) which in turn is close to the maximum of tetrads CAAC, as shown in Fig. 3. Assuming further that $k_{CAAC} = 1.5 \times 10^{-3}$, chosen after a trial and error process for the solvent mixture with 60% THF, the calculated values illustrated in Fig. 4 are obtained which are close to the experimental uncorrected values. A similar result may be obtained for the solvent mixtures with 81% THF. If the corrected values of k_0 are considered, the difference between the solvent mixtures are not very large and an average calculated curve may be obtained (Fig. 5) assuming $k_{AAA} = 2.0 \times 10^{-3}$, $k_{CAC} = 3 \times 10^{-3}$, $k_{CAAA} = 4 \times 10^{-3}$ and $k_{CAAC} = 15 \times 10^{-3}$. It may be concluded that consideration of the sequence distribution allows a reasonable account of the initial methanolysis rate of the vinyl chloride copolymers.

The last column of Table 1 gives the acceleration degree m, obtained from the slopes of the straight lines drawn in a plot of the rate constant k vs time:

$$k = k_0\left(1 + m\frac{\{A\}}{\{A_0\}}\right)$$

where $\{A\}$ and $\{A_0\}$ are the actual and initial concentrations of A units, respectively.

As in the case of homopolymers, the acceleration degree decreases with the increasing THF content of the solvent mixtures. It also greatly decreases with increasing chlorine content of the copolymer. This decrease may be compared with the decrease of the fraction of A units in sequences longer than 5 as shown by comparing Figs. 6 and 7. However, comparison of Runs 3 and 23 shows that it is strongly dependent on the molecular weight. Also, although the copolymer of Run 12 is rich in C units and contains practically no A sequences longer than 4, a slight acceleration may be observed. In the previous paper the acceleration was interpreted as being caused by the progressive trapping of the catalyst cation in the dissolved polymer sphere. The efficiency of this trapping may be higher if the polymer sphere is more compact; however, if the molecular weight of the copolymer is low (solution copolymerization) because of the smaller size of the sphere, the efficiency of the trapping remains low and the catalyst may diffuse out easily toward the solvent mixture. Of course, the sequence distribution is also important because a cation released after a set of elementary steps of a methanolysis reaction can escape more easily if it is not immediately captured by an adjacent acetate unit.

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