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Vinyl Chloride-Vinylidene Chloride Copolymerization in Strong Donor Solvents: A New Interpretation of Structural Defects

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ABSTRACT

Penultimate effects detected on the vinylidene chloride-ended radical in the vinylidene chloride-vinyl chloride copolymers prepared in tetrahydrofuran had previously been interpreted in terms of head-to-head addition. But new ^{1}H-NMR analysis of the homopolymers and copolymers synthesized in proton-donor and inert solvents suggest these effects, giving abnormal structures, might be due to the proton-transfer reactions, particularly in strong proton-donor solvents. Chain transfer reactions have been found degradative, so the overall polymerization rate is drastically decreased.

INTRODUCTION

In a previous paper [1] it was assumed that the penultimate effect detected with the vinylidene-ended radical in the vinyl chloride (C)-vinylidene chloride (V) radical copolymerization carried out in tetrahydrofuran (THF) might be interpreted in terms of head-to-head

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addition of a V molecule to a C-ended radical. This explanation was based on the ^1H-NMR analysis of the C-V copolymers. Indeed, the spectra of these copolymers show the (α_H) triplet at 5.9 ppm, which has been assigned to the $\sim\sim CH_2-\underline{CH}Cl-CCl_2\sim\sim$ structure due to the head-to-head addition. Then, this anomalous propagation was shown to involve a new but complicated kinetical scheme which should be described by a copolymerization equation close to the penultimate model. Moreover, it was interesting to note a good evidence for either the initial copolymer composition or several functions of the sequence distribution, depending on choice of the penultimate model or the head-to-head addition model. This model has been already suggested by several authors [2, 3] who interpreted some resonances near the methylene resonance of vinylidene chloride as tail-to-tail sequence structures due to head-to-head additions in C-V copolymerization. Moreover, the methylene resonances are sensitive to tetrad sequence distributions [4-6].

The purpose of this study is to show, by proton NMR analysis of the homo- and copolymers, that these structural defects should originate from proton transfer reactions, particularly, if strong proton-donating agents, such as n-butyraldehyde or tetrahydrofuran, are used. On the other hand, one does not observe any structural defects in copolymers obtained in a weak proton donor like dioxane.

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EXPERIMENTAL

Monomers and solvents were freshly distilled and stored under an inert atmosphere. The homopolymers and copolymers were prepared by using AIBN initiator according to the classical technique [1] at 60°C.

The ^1H-NMR spectra of homopolymer and copolymer were recorded from hexachloroacetone or o-dichlorobenzene solutions at 130-140°C by using a Varian DA 60 IL spectrometer and a Jeol JRA A1 spectrum accumulator.

RESULTS AND DISCUSSION

Figure 1 presents the ^1H-NMR spectrum of a vinylidene-rich C-V copolymer prepared in THF. It shows clearly the α_H triplet centered at 5.9 ppm which was assigned to the structure

$$\sim\sim CH_2-\underline{CH}Cl-CCl_2\sim\sim$$

I

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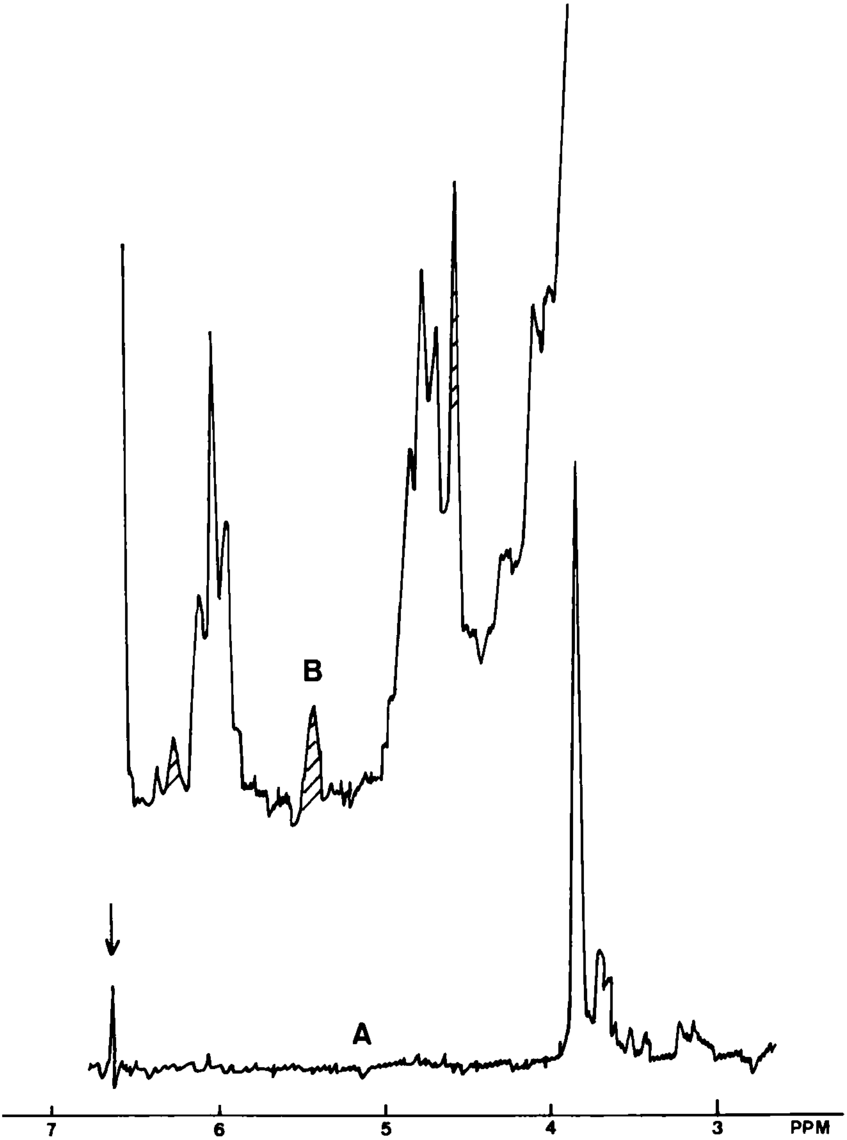

FIG. 1. ^{1}H-NMR spectra of vinyl chloride-vinylidene chloride copolymer with 90% vinylidene chloride: (A) single scan spectrum; (B) accumulated spectrum (256 scans). Solvent, hexachloroacetone; T, 130°C.

if head-to-head addition is assumed [1]. Quantative analysis of this structure versus the total amount of vinyl chloride showed that this proportion became very weak in vinyl chloride-rich C-V copolymers; the abnormal propagation only concerned the V monomer addition to a C-ended radical.

Our previous NMR studies dealt only with C-V copolymers prepared in THF, but in a further analysis of dichloroethane-prepared copolymers (70% V) the α_H triplet did not appear. It was therefore necessary to verify the existence of such a structure in copolymers prepared in different solvents.

Dioxane, a weakly polar solvent was chosen; the kinetic data for the C-V copolymerization are reported in Table 1. The corresponding Fineman-Ross plot is given in Fig. 2 and compared with those obtained in THF or in bulk copolymerization. A departure from the theoretical straight line in V-rich monomer feed is noteworthy, this curvature being more pronounced as the amount of V increases.

In the NMR spectra of these copolymers, no α_H triplet was observed (Fig. 3). From these results, the α_H triplet must be assigned to another protonated structure, probably one due to the proton transfer reaction from the solvent to macroradicals.

In order to support this new assumption, two series of NMR analyses were achieved: (1) the analysis of C-V copolymers prepared in solvent mixtures with increasing amounts of proton donor solvent, such as THF or butyraldehyde (BuA); (2) the analysis of poly(vinylidene chloride) or poly(vinyl chloride) prepared in various proton donor solvents such as THF, butyraldehyde, or dioxane. The kinetic data for copolymerizations carried out in pure donor solvents or in solvent mixtures are reported in Table 2. From the values presented, it seems obvious that the structural defect formation depends on the composition of the reaction mixture, since the greater the THF (or butyraldehyde) proportion, the higher the structure proportion in C-V copolymers (approximately prepared with the same monomer feed). The greatest proportion of defects corresponds to BuA solvent mixtures. Actually with V/(BuA) = 0.4, one obtains the highest proportion (32%); the same proportion required, for THF mixtures, a V/THF ratio of 0.1. Thus it seems that the existence of these defects depends on the proton-donating power of the solvent.

With regard to the homopolymers prepared either in THF or BuA, the corresponding spectra give an α_H triplet centered at 5.9 ppm for the PV (Fig. 4) and near 3.5 ppm for PC (Fig. 5). In the dioxane-prepared homopolymer spectra, there is no α_H triplet (Fig. 3). Because no head-to-head addition is possible in V or C polymerization, the α_H triplet can only originate from the following structures:

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TABLE 1. Kinetic Data for Vinyl Chloride (C)-Vinylidene Chloride (V) Copolymerization in Dioxane at 60°C

Copolymers	C (mole)	V (mole)	Solvent (mole)	$x_c = C/V$ (monomer feed)	$\Delta\rho_c \times 10^2$ (%/min)	$\Delta\rho_v \times 10^2$ (%/min)	$n_c = C/V$ in copolymers
1	0.178	1.05	4.4	0.169	8.4	11.8	0.12
2	0.760	0.13	3.4	5.82	8.6	30.0	1.67
3	0.64	0.408	4.4	1.57	3.03	16.9	0.286
4	0.061	0.645	2.72	0.098	16.5	12.4	0.130
5	0.022	0.865	4.15	0.0254	14.7	15.1	0.0278
6	1.24	0.046	4.75	27.0	10.5	40.0	7.10
7	0.315	0.963	4.75	0.336	6.80	12.5	0.184
8	0.228	0.835	4.20	0.0525	20.0	15.5	0.068

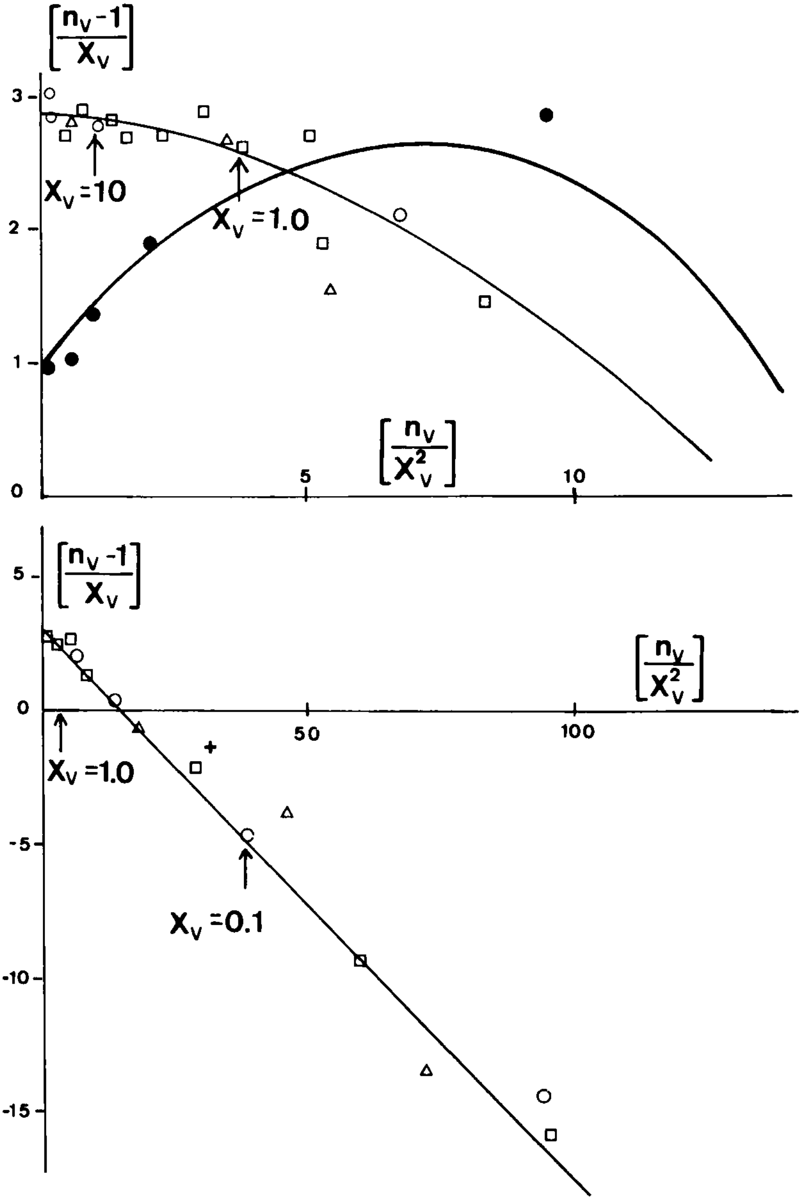

FIG. 2. Fineman-Ross plots for vinyl chloride-vinylidene chloride copolymerization: (□) data of Enomoto [4]; (+) data of Agron [7]; (△) data of Germar [8]; (○) this study, in THF; (●) this study in dioxane.

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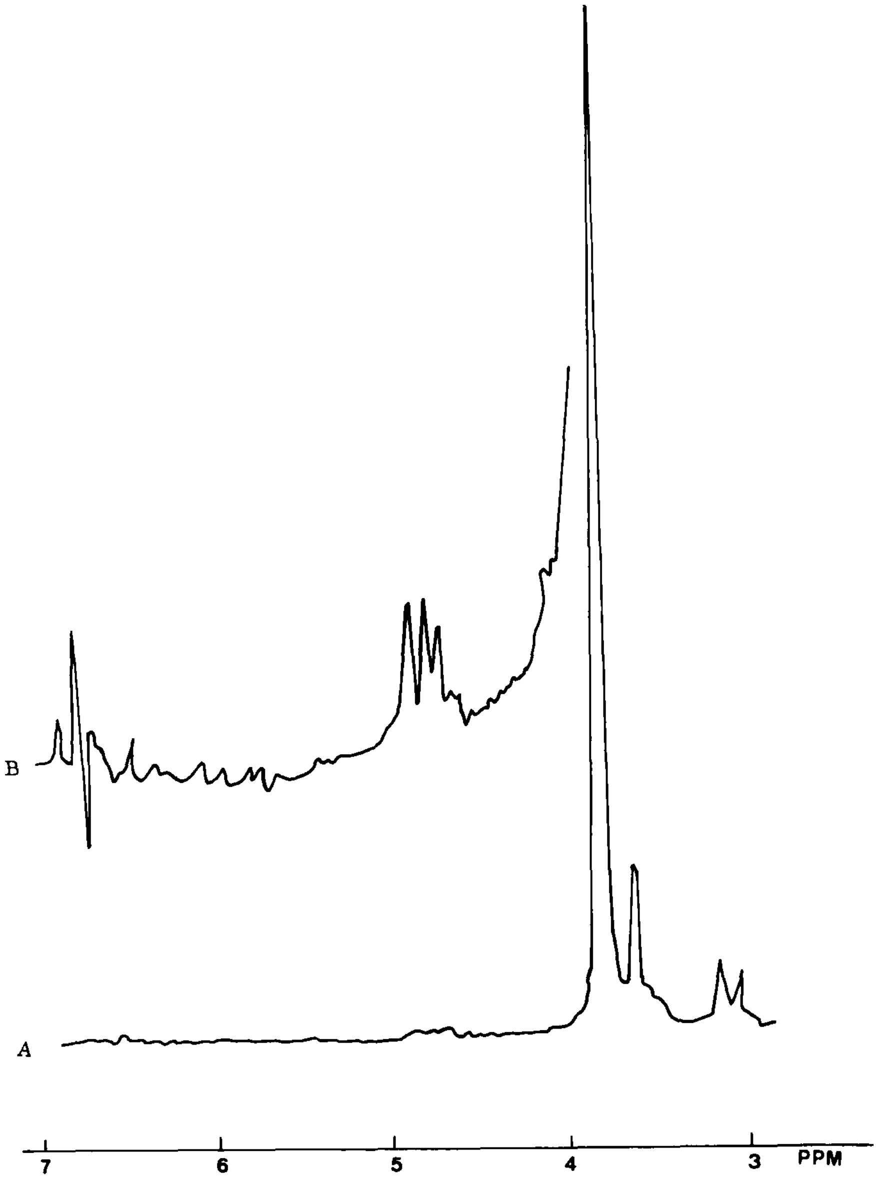

FIG. 3. ^{1}H-NMR spectra of vinylidene homopolymer prepared in dioxane mixture: (A) accumulated spectrum (256 scans); (B) enhanced spectrum. Solvent, hexachloroacetone.

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TABLE 2. Influence of the Solvent on the Amount of Abnormal Structures in Vinyl Chloride (C)-Vinylidene Chloride (V) Copolymerization

Solvent (S)	Temperature (°C)	$x_c = C/V$ (mole/mole)	Composition of the monomer feed C-V (mole %)	(V)/(S) (mole/mole)	Abnormal structures vs. C in the copolymers (mole %)	Copolymer composition C-V (mole %)	M_n (osmometry)
THF	60	0.34	25.5-74.5	0.120	33.5	7.5-92.5	1500
THF	30	0.34	25.5-74.5	0.126	33.6	7.7-92.3	1200
THF	80	0.373	27.2-72.8	0.101	34.5	4.4-95.6	900
Dioxane	60	0.336	25-75		0		2300
THF + Dioxane (5 mole % THF)	60	0.370	26.8-73.2	2.600	7.4	6.1-93.9	1200
THF + Dioxane (30 mole % THF)	60	0.345	25.8-74.2	0.420	21	7-93	1050
Butyraldehyde + Dioxane (5 mole % butyraldehyde)	60	0.830	46-54	1.70	7.4	17.6-82.4	600
Butyraldehyde + Dioxane (15 mole % butyraldehyde)	60	0.760	43-57	0.52	27.5	15.3-84.7	700
Butyraldehyde + Dioxane (40 mole % butyraldehyde)	60	0.780	43.5-56.5	0.130	32.5	17.5-82.5	350

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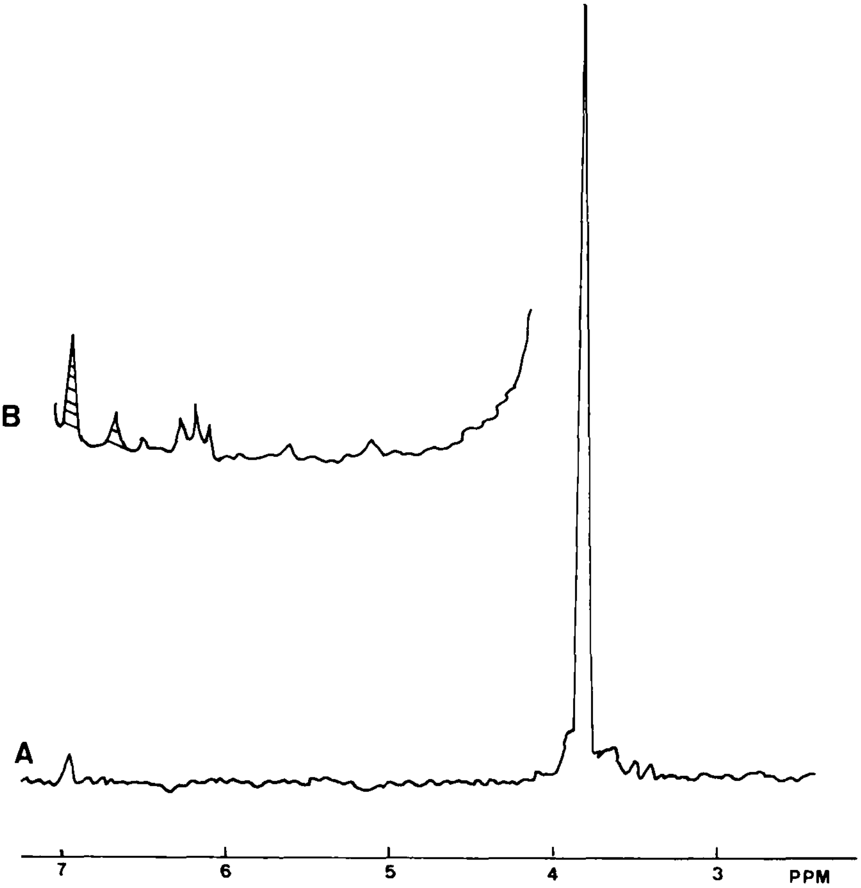

FIG. 4. ^{1}H-NMR spectra of vinylidene homopolymer prepared in THF mixture: (A) accumulated spectrum (256 scans); (B) enhanced spectrum. Solvent, hexachloroacetone.

$\sim CH_2-CCl_2-CH_2-\underline{CH}Cl_2$ (5.9 ppm) for PV

II

and

$\sim CH_2-CHCl-CH_2-\underline{CH_2}Cl$ (3.5 ppm) for PC

III

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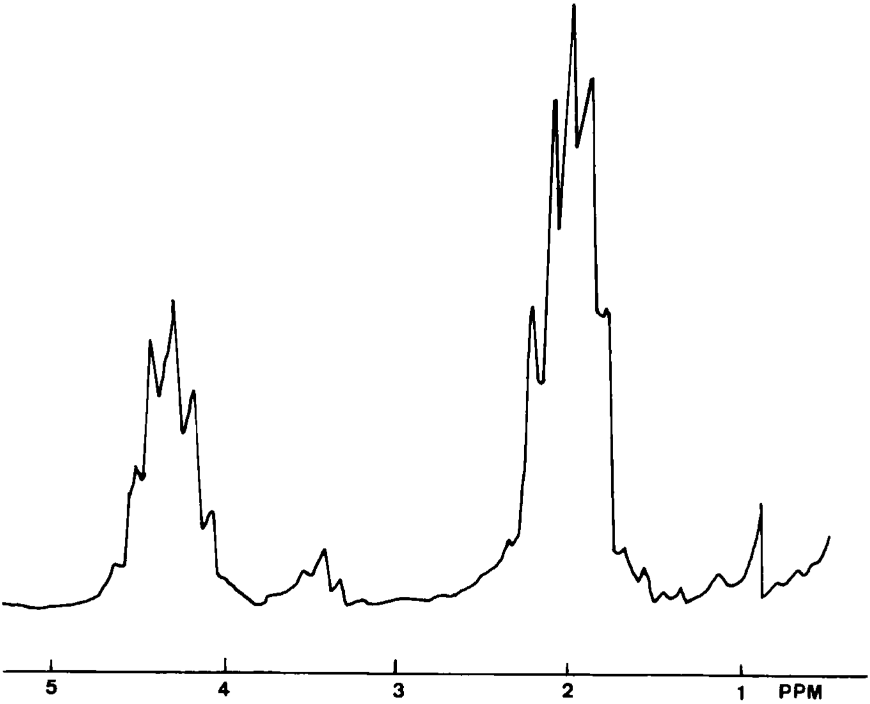
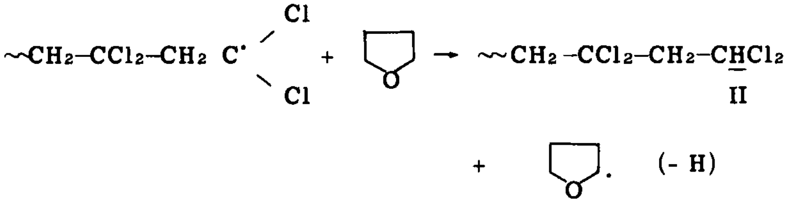
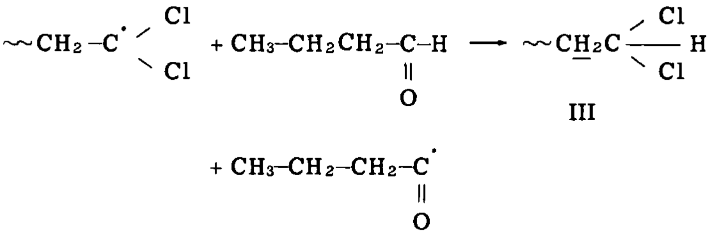


FIG. 5. ^{1}H-NMR spectra of vinyl chloride homopolymer prepared in THF mixture. Solvent, o-dichlorobenzene.

Chain end II which is in fact two doublets, has been found in PC obtained in CCl_4 with the $TiOBu_4$-$AlEt_3$ catalyst system [9]. Chain end III is a triplet observed in PC obtained in THF with tert-BuMgCl catalyst [10].

The proton transfer mechanisms between strong proton donor solvents (THF or butyraldehyde) and macroradicals are as follows [11]:





For C-V copolymers, the triplet centered at 3.5 ppm is not observed because of the overlapping of the methylene resonances of short PV homosequences in the copolymers (Fig. 1).

From the molecular weights reported in Table 2, in the last column, it is possible to estimate with some accuracy the THF transfer constant related to V-ended radical:

$C_s(\text{THF}) \sim 0.12$ for PV

$C_s(\text{THF}) \sim 0.0024$ for PC

In butyraldehyde, $C_s = 0.011$ for PC [12], whereas its value for PV from a rough determination is probably higher.

These values assume a strong proton-donating power for both solvents; it may be noted that the transfer is degradative with THF because the transferred radical cannot initiate the polymerization. No THF residue was detected in C-V copolymers or homopolymers analyzed by IR [13]. In butyraldehyde, the transfer is also degradative, although the new radical initiates the polymerization to a small extent, because a small IR absorption is found near 1720 cm^{-1} (C=O) in C-V copolymers, which, then, implies a decreasing initiation rate. This could be due to an important termination rate of the primary radicals. The observed polymerization rate is lower in BuA than in THF.

Figure 6, on which the initial consumption rates for V and C monomers have been plotted versus the monomer feed composition confirms this degradative transfer assumption quite well. Indeed, it may be observed that the monomer consumption rates decrease drastically in THF over the whole range of composition, except for V in C-rich monomer feed.

In dioxane, a weak proton-donating solvent, one has again the same phenomenon of minimum polymerization rates [14], but these latter are higher.

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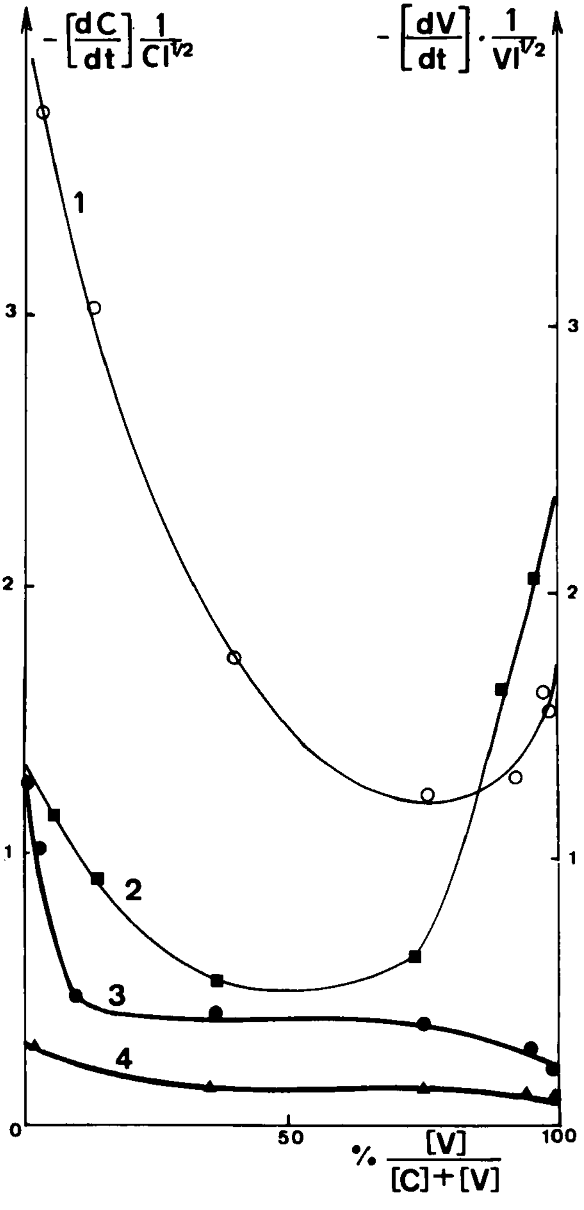

FIG. 6. Initial rate of consumption of vinyl chloride (C) and vinylidene chloride (V) monomer vs. composition of monomer feed; (1) V, in dioxane; (2) C, in dioxane; (3) V, in THF; (4) C, in THF. I denotes initiator concentration.

CONCLUSION

It may be concluded therefore that the head-to-head addition previously assumed could not actually occur to an important extent, but that the established mechanisms and copolymerization equations [1] remain valid for other systems. The chain transfer reaction between proton donor solvents and macroradicals should be the main explanation of the structural defect found in vinyl chloride-vinylidene chloride copolymers.

With the transfer reagents used in this study, the chain transfer reactions were found to be degradative. The reactivity of the transferred radical was lower. Consequently, the overall polymerization rate drastically decreases. Such a phenomenon has been observed in homopolymerization by Deb [15], who proposed kinetic relationships describing this special case of nonideal polymerization. Nevertheless, more kinetical measurements (chiefly polymerization rates) should be useful to apply this method to copolymerizations with degradative transfer and to deduce the suitable relationships. However, chain-transfer reactions should not be the only causes of the kinetic deviations observed in both strong and weak donor solvents or in bulk copolymerization.

To confirm our assumption, some complexation phenomena between vinyl chloride and vinylidene chloride and donor solvents that have been studied will be published in the near future.

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REFERENCES

[1] A. Guyot, C. Pichot, J. Guillot, and Q. T. Pham, *J. Macromol. Sci.-Chem.*, **A6**, 1681 (1972).

[2] R. Chujo, S. Satoh, and E. Nagai, *J. Polym. Sci. A*, **2**, 285 (1964).

[3] J. L. McClanahan and S. A. Previtera, *J. Polym. Sci. A*, **3**, 3919 (1965).

[4] V. U. Johnsen, *Kolloid Z.*, **210**, 1 (1966).

[5] S. Enomoto and S. Satoh, *Kolloid Z.*, **219**, 12 (1967).

[6] Y. Yamashita and K. Ito, *Macromolecules*, **1**, 529 (1968).

[7] P. Agron, T. Alfrey, T. Bohrer, H. Nass, and N. Wechsler, *J. Polym. Sci.*, **3**, 157 (1948).

[8] V. H. Germar, *Makromol. Chem.*, **84**, 36 (1965).

[9] Q. T. Pham, P. Rocaniere, and A. Guyot, *J. Appl. Polym. Sci.*, **14**, 1291 (1970).

[10] Q. T. Pham and M. Taieb, *J. Polym. Sci. A-1*, 1099 (1970).

[11] I. Rosen, P. H. Burleigh, and J. F. Gillespie, *J. Polym. Sci.*, **54**, 31 (1961).

[12] M. Imoto, K. Takemoto, and Y. Nakai, *Makromol. Chem.*, **48**, 80 (1961).

[13] H. S. Mickley, A. S. Michaels, and A. L. Moore, J. Polym. Sci., 60, 121 (1962).
[14] W. I. Bengough and R. G. W. Norrish, Proc. Roy. Soc. (London), A 220, 155 (1953).
[15] P. C. Deb, Eur. Polym. J., 11, 31 (1974).

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