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

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To cite this Article Pichot, C. , Guillot, J. , Pham, Q. T. and Guyot, A.(1973) 'Internal Transfer Reactions in the Copolymerization of Vinyl Acetate with Chlorinated Monomers', Journal of Macromolecular Science, Part A, 7: 2, 495 — 512

To link to this Article: DOI: 10.1080/00222337308061151

URL: http://dx.doi.org/10.1080/00222337308061151

J. MACROMOL. SCI.—CHEM., A7(2), pp. 495-512 (1973)

Internal Transfer Reactions in the Copolymerization of Vinyl Acetate with Chlorinated Monomers

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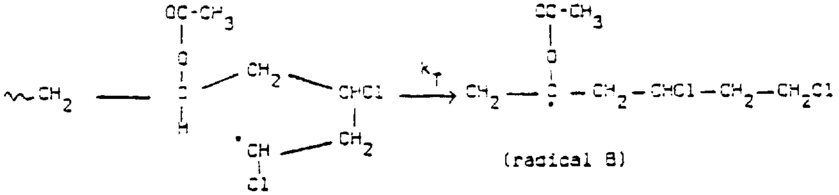
ABSTRACT

In the copolymerization of vinyl acetate (A) with either vinyl chloride (C) or vinylidene chloride (V), an internal transfer (backbiting) reaction—of the C- or V-ended radicals on an antepenultimate A unit—is proposed to be responsible for the deviation of the copolymerization kinetics from the Lewis and Mayo theory. The deviations disappear if A is replaced by isopropenylacetate [I_p]. Then one gets, for the I_p-C copolymerization, $r_{I_p} = 0.35$ and $r_c = 2.4$, and for I_p-V copolymerization, $r_{I_p} = 0.13$ and $r_V = 5.9$. The internal transfer reaction causes the formation of branches which may be evidenced by NMR analysis of constant composition suspension A-C copolymers. A kinetic scheme is proposed and the corresponding reactivity ratios derived $r_A = 0.29$, $r_C = 1.60$, $r_B = 0.3$ (radical resulting from the transfer reaction), and $k_T = 1500$ (rate constant of the transfer reaction at 50°C). The distribution of

branches is calculated together with the sequence distribution functions for the A or C units.

INTRODUCTION

In a previous paper [1], the kinetics deviations from the Lewis and Mayo theory observed in the copolymerization of vinyl acetate (A) with either vinyl chloride (C) or vinylidene chloride (V) have been interpreted in terms of an antepenultimate effect on the chlorinated unit ended radicals. The corresponding reactivity ratios for A-C copolymerization were $r_A = 0.29$, $r_{CCC} = 1.67$, $r_{ACC} = 4.6$, and $r_{AC} = 2.05$, and for V-C copolymerization $r_A = 0.07$, $r_{VVV} = 5.30$, $r_{AVV} = 11.5$, $r_{AAV} = 8.0$, and $r_{VAV} = 6.0$. It has been suggested further that these antepenultimate effects might be caused by an internal transfer reaction involving the tertiary hydrogen atom of an antepenultimate vinyl acetate unit



Such a back-biting reaction is commonly proposed to explain the presence of short branches in high-pressure polyethylene, or ethylene-vinyl acetate copolymers [2].

The purpose of the present paper is to describe experiments which support this assumption and to present a new kinetic scheme involving three radicals (the two regular V-ended and C-ended radicals, and the branched radical B) and the transfer rate constant k_T.

First, the vinyl acetate monomer has been replaced by isopropenyl acetate (I_p) where the tertiary hydrogen atom of the A unit is replaced by a methyl group, and the copolymerization kinetics with V or C have been studied. Second, the presence of branches has been confirmed by NMR analysis of the amount of chloromethyl groups, CH_2Cl.

COPOLYMERIZATION OF ISOPROPENYL ACETATE

The experiments were carried out in dimethyl formamide solutions (sometimes cyclohexanone) at 60°C using azobisisobutyronitrile as

TABLE 1. Charges and Kinetic Results in the Copolymerization of Vinyl Chloride (C) and Isopropenyl Acetate (I_p)

C (moles)	I_p (moles)	Solvent	$x_c = C/I_p$	$n_c = dC/dI_p$
0.290	0.731	5.73	0.396	0.95
0.785	0.167	5.75	4.70	10.80
0.760	0.088	5.73	8.60	21.80
1.02	0.070	5.17	14.80	35.80
0.735	0.031	5.50	23.50	56.50
0.720	0.021	5.50	34.0	81.50

TABLE 2. Charges and Kinetic Results in the Copolymerization of Vinylidene Chloride (V) and Isopropenyl Acetate (I_p)

V (moles)	I_p (moles)	Solvent	$x_v = V/I_p$	$n_v = dV/dI_p$
0.310	0.417	5.55	0.75	4.57
0.522	0.300	5.55	1.73	14.00
0.680	0.182	5.42	3.73	22.00
0.690	0.060	5.66	11.63	69.20
0.700	0.040	4.10	18.50	106.5
0.760	0.023	3.90	33.10	198

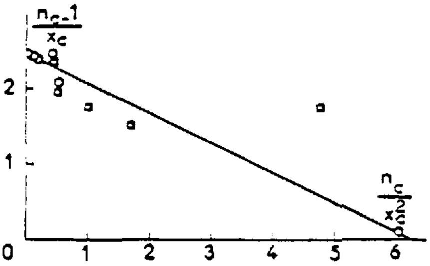


FIG. 1. Fineman-Ross plot for vinyl chloride (C)-isopropenyl acetate copolymerization. (□) Data from Smets [5], (o) this study.

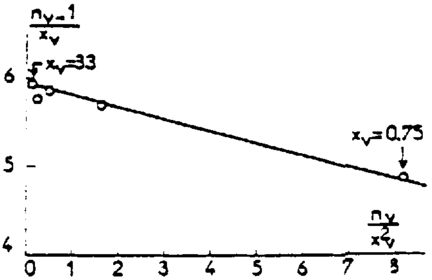


FIG. 2. Fineman-Ross plot for vinylidene chloride (V)-isopropenyl acetate copolymerization.

initiator. The kinetics are studied using the gas chromatographic method previously described [3]. The initial charges and kinetics results are reported in Tables 1 and 2, respectively, for the I_p-C and I_p-V systems. The corresponding Fineman-Ross plots [4] are shown in Figs. 1 and 2, respectively. Some data reported by Hard and Smets [5] are included in Fig. 1. It appears that the kinetic deviations from the Lewis and Mayo theory which have been observed for the corresponding copolymerizations of vinyl acetate do not occur with isopropenyl acetate, although the experiments involve extreme composition of the monomer feed. These results strongly support our assumption that the deviation are caused by the back-biting reaction. The following reactivity ratios may be derived from the plots of Figs. 1 and 2.

For the vinyl chloride-isopropenyl acetate copolymerization, r_p = 0.35 ± 0.1 and r_c = 2.4 ± 0.1. These values are in rather good agreement with the literature data of r_{I_p} = 0.25 and r_c = 2.2 [5, 6].

For the vinylidene chloride-isopropenyl acetate, there are no data in the literature and our results are r_{I_p} = 0.13 and r_v = 5.9 ± 0.1.

It may be noted also that the isopropenyl acetate is a poorly reactive monomer, probably because it is resonance-stabilized, as already suggested by Smets [5]. For this reason the yield becomes very low when the concentration of that monomer increases and the kinetic results are not accurate enough to give precise results concerning the composition of the I_p- rich copolymers. For this reason, and because kinetics deviation were expected in the other part of the range, we have carried out only a few experiments with low values of x_c or x_v.

NMR STUDY OF BRANCHING

The back-biting reaction of a vinyl chloride-ended radical on an antepenultimate vinyl acetate unit is expected to lead to a $-CH_2-CH_2Cl$ chain-end in the short branch. However, this chain end structure may also arise from transfer reactions of the same radical either with monomer or solvent. Especially the dimethyl formamide solvent, which has been used in previous experiments [1], is a powerful transfer agent like other solvents such as tetrahydrofuran. It was then decided to prepare a new set of copolymers using a suspension technique. The experiments were carried out at 50°C in a glass and metal autoclave stirred magnetically (Ingenieur-Bureau, Zurich), using azobisisobutyronitrile as initiator and a mixture of polyvinyl alcohol (1 g) and hydroxymethylcellulose (0.25 g) as protective colloid. Owing to the reactivity ratios of this system (r_c = 2.0 r_A = 0.29) the vinyl chloride monomer tends to be consumed more rapidly, so that the pressure in the autoclave tends to decrease. The experiments were carried out under constant pressure by using a special device which involves a Bourdon manometer coupled with a photoelectric cell sensitive to the change of position of the needle of the manometer. The cell governs an electromagnetic valve between the autoclave and a vinyl chloride reservoir. The constant pressure corresponds roughly to a constant composition of the monomer feed and allows a copolymer with constant composition to be obtained. The characteristics of the copolymerization and of the copolymer obtained are given in Table 3. The copolymer compositions were derived from the NMR spectra using the well resolved

TABLE 3. Constant Pressure Copolymerization of Vinyl Acetate and Vinyl Chloride and Data about the Copolymers

Run No.	Monomer feed composition (mole %) C	A	Pressure (kg/cm^2)	Copolymer composition (mole %) C	A	(η) THF (25°C)	$\overline{M}_n$	CH_2Cl α_C	$\overline{P}_n$	K_T
1	12	88	0.85	30	70	217	109,500	0.005	-	-
2	27	73	1.82	53	47	99	67,200	0.0095	95	1400
3	47.5	52.5	3.30	70	30	-	47,700	0.0055	100	1460
4	61.5	38.5	4.45	77.5	22.5	75.4	36,000	0.0037	165	1510
5	85	15	5.80	87.0	13.0	95.1	52,500	0.0051	120	7300

α-methine protons [7] at 4.9 τ (A units) and 5.8 τ (C units), or, for the extreme parts of the range, from a comparison of the α-methine protons of the more abundant unit and the total of the methylene and methyl protons between 7.5 and 8.2 τ (spectra recorded at 60 Mc in o-dichlorobenzene or o-dichlorobenzene-hexachloracetone mixtures at 140°C by a Varian DA 60-IL spectrometer, hexamethyldisiloxane being the internal reference). These compositions were checked by measuring the carbon and chlorine contents. The molecular weight were estimated from viscosity-gel permeation chromatography experiments.

It has been shown previously [8] that the protons of the chloromethyl group of a $-CH_2-CH_2Cl$ chain end resonate as a triplet at 6.5 τ. Such a triplet appears clearly after spectrum accumulation (Jeol JR-A1) as shown in Fig. 3. From the area under the triplet and the area of the α-methine protons of the C units (αC protons centered at 5.8 τ), one gets the proportion of the C units engaged as chain-end or branches-end. The corresponding values between

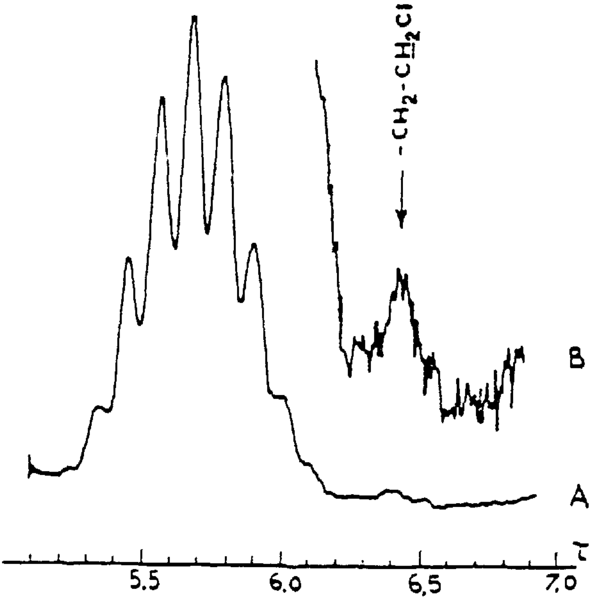


FIG. 3. Accumulated NMR spectrum (128 scans) of a vinyl chloride (53%)-vinyl acetate (47%) suspension copolymer showing the resonances of the α-methine protons of the (A) vinyl chloride units (5.8 τ) and the (B) chloromethyl protons (6,5 τ).

0.5% and about 1% are given in Table 3. Assuming there are no branches and a random termination process, it is possible to calculate from the NMR data and the copolymer composition a number-average polymerization degree $\overline{P_n}$, also shown in Table 3. Comparison of $\overline{P_n}$ with the estimated $\overline{M_n}$ from molecular weight measurement shows clearly that there are many branches in each molecule. Chloromethyl groups have been verified to be present in the copolymers obtained from copolymerization experiments in solution; however, in these cases, the contribution of the chain ends is important, and precise measurements of $\overline{M_n}$ are necessary to decide on the existence of branches. Moreover, NMR measurements might be wrong because the α-methyl resonances of C are perturbed by the first-order triplet of the saturated acetyl chain-end ($-CH_2-CH_2-OCOCH_3$) centered at 6.1 τ. However, analysis of the suspension copolymers clearly confirms the presence of the branches expected from the assumption of the back-biting reaction.

KINETIC INTERPRETATION OF THE RESULTS

On the basis of the above results it is possible to build a new kinetic scheme, which, for reasons of simplicity, rules out any penultimate effect and assumes only the regular head-to-tail propagation reaction and an internal transfer reaction. This transfer reaction is assumed to occur between a C-ended radical and an antepenultimate vinyl acetate unit, whatever the nature of the penultimate unit. The scheme also involves the reactivity of the radical B resulting from the transfer reaction be different from that of a regular A-ended radical. The following reactions are to be considered:

$$A^{\circ} + A \xrightarrow{k_{aa}} \sim AA^{\circ} \equiv A^{\circ} \tag{1}$$

$$A^{\circ} + C \xrightarrow{k_{ac}} \sim AC^{\circ} \equiv C^{\circ} \tag{2}$$

$$AA^{\circ} + A \xrightarrow{k_{aa}} \sim AA^{\circ} \equiv A^{\circ} \tag{3}$$

$$AA^{\circ} + C \xrightarrow{k_{ac}} \sim AAC^{\circ} \equiv C^{\circ} \tag{4}$$

$$AC^{\circ} + A \xrightarrow{k_{ca}} \sim A^{\circ} \tag{5}$$

$$AC^{\circ} + C^{\circ} \xrightarrow{k_{cc}} \sim ACC^{\circ} \equiv C^{\circ} \tag{6}$$

$$AAC^{\circ} \xrightarrow{k_T} \sim B^{\circ} \tag{7}$$

$$ACC^{\circ} \xrightarrow{k_T} \sim B^{\circ} \tag{8}$$

$$B^{\circ} + A \xrightarrow{k_{ba}} \sim A^{\circ} \tag{9}$$

$$B^\circ + C \xrightarrow{k_{bc}} \sim C^\circ \tag{10}$$

$$AAC^\circ + A \xrightarrow{k_{ca}} \sim A^\circ \tag{11}$$

$$AAC^\circ + C \xrightarrow{k_{cc}} \sim C^\circ \tag{12}$$

$$ACC^\circ + A \xrightarrow{k_{ca}} \sim A^\circ \tag{13}$$

$$ACC^\circ + C \xrightarrow{k_{cc}} \sim C^\circ \tag{14}$$

$$C^\circ + A \xrightarrow{k_{ca}} \sim A^\circ \tag{15}$$

$$C^\circ + C \xrightarrow{k_{cc}} \sim C^\circ \tag{16}$$

As usual, one defines the reactivity ratios for each of the three radicals:

$$r_A = k_{aa}/k_{ac}, \qquad r_B = k_{ba}/k_{bc}, \qquad r_C = k_{cc}/k_{ca}$$

The equation giving $n = dA/dC$ as a function of $x = A/C$ may be derived, as usual, from the expression of the rate of consumption of each monomer, $- dA/dt$ and $- dC/dt$, using the steady-state assumption for any of the three radicals:

$$dA^\circ/dt = 0 = k_{ca}C^\circ A + k_{ba}B^\circ A - k_{ac}A^\circ C \tag{17}$$

$$dC^\circ/dt = 0 = k_{ac}A^\circ C + k_{bc}B^\circ C - k_{ca}C^\circ A - k_T(AAC^\circ + ACC^\circ) \tag{18}$$

$$dB^\circ/dt = 0 = k_T(AAC^\circ + ACC^\circ) - k_{ba}B^\circ A - k_{bc}B^\circ C \tag{19}$$

and

$$- dA/dt = k_{ca}C^\circ A + k_{aa}A^\circ + k_{ba}B^\circ A \tag{20}$$

$$- dC/dt = k_{cc}C^\circ C + k_{ac}A^\circ C + k_{bc}B^\circ C \tag{21}$$

Using Eqs. 17-19, one obtains

$$n = \frac{dA}{dC} = \frac{k_{aa}A^\circ A + k_{ac}A^\circ C}{k_{cc}C^\circ C + k_{ca}C^\circ A + k_T(AAC^\circ + ACC^\circ)} \tag{22}$$

Using the complete scheme (Eqs. 1-16) and the steady-state assumption for any radicals, the final expression of n is

$$n = \frac{1 + r_A x}{(1 + r_C/x)\left[1 - \frac{\alpha\gamma}{\beta}\frac{k_T}{k_{cc}C}\right] + \frac{\gamma}{\beta}\frac{k_T}{k_{cc}C}} \tag{23}$$

with

$$\alpha = \frac{r_B x}{1 + r_B x}, \qquad \beta = 1 + \frac{x}{r_C} + \frac{k_T}{k_{cc}C}, \qquad \gamma = r_A x + \frac{r_C}{r_C + x}$$

Equation (23) is much too complex to be used directly. However it may be seen that when $x \to 0$, $n/x \to 1/r_C$, and when $x \to \infty$, $n/x \to r_A$.

Using the data previously published [1], the plots of n/x vs x or 1/x, shown in Figs. 4 and 5, respectively, lead to $r_A = 0.29 \pm 0.02$ and $r_C = 1.60 \pm 0.05$.

The value of the reactivity ratio corresponding to the branched radical r_B may be estimated to be close to that obtained for the isopropenylacetate-ended radical in the I_p-C copolymerization where the methyl group replaces the short branch. It is also expected to be

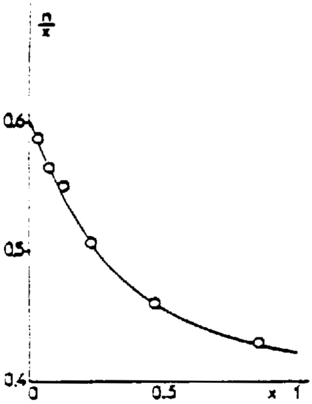


FIG. 4. Vinyl chloride (C)-vinyl acetate (A) copolymerization. Plot of n/x vs x. n = dA/dC. x = A/C.

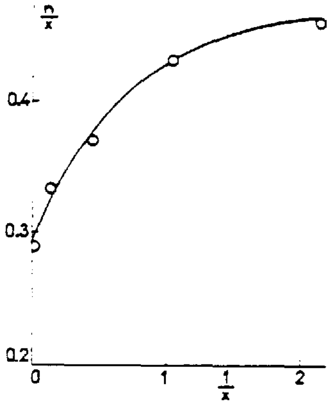


FIG. 5. Vinyl chloride (C)-vinyl acetate (A) copolymerization. Plot of n/x vs 1/x. n = dA/dC. x = A/C.

close to the value of r_A, for which the branch is replaced by a hydrogen atom. Thus it seems reasonable to adopt $r_B = 0.3$.

The value of k_{cc}, the propagation rate constant of the homopolymerization of vinyl chloride, is given in the literature [9] as $k_{cc} = 11{,}000$ at 50°C. It remains to estimate k_T. Because the suspension copolymerization has been carried out under constant composition conditions, the ratio $[CH_2Cl]/[C]$ given in Table 3 from NMR results may be related directly to kinetic data. From Eqs. [7] and [8]:

$$d[CH_2Cl]/dt = k_T[AAC^\circ + ACC^\circ] \tag{24}$$

Equation (24) assumes the chloromethyl groups from intermolecular transfer reaction to be negligible. The molecular weight data show that such an assumption does not exceed the experimental error in NMR measurements. From the expression of -dC/dt:

$$-\frac{d(CH_2Cl)}{dC} = \frac{(CH_2Cl)}{\alpha_C} = \frac{k_T(AAC^\circ + ACC^\circ)}{k_{cc}C^\circ C + k_{ca}C^\circ A + k_T(AAC^\circ + ACC^\circ)} \tag{25}$$

$$\frac{CH_2Cl}{\alpha_C} = \frac{1}{\left(1 + \frac{r_C}{x}\right)\left[\left(\frac{\beta}{\gamma k_T/k_{cc}\,C}\right) - \alpha\right] + 1} \qquad (26)$$

The value of the transfer constant may then be deduced as

$$\frac{k_T}{k_{cc}} = \frac{C\left(\frac{x}{r_C} + 1\right)}{\dfrac{1 + \left[\dfrac{CH_2Cl}{\alpha_C}\right]\left[\left(1 + \dfrac{r_C}{x}\right) - 1\right]}{\left[\dfrac{CH_2Cl}{\alpha_C}\right]\left(1 + \dfrac{r_C}{x}\right)} - 1} \qquad (27)$$

The values of k_T calculated for each copolymer are given in the last column of Table 3. In the middle range where the experimental errors are not too large, it is reasonably constant around 1500. It corresponds to the transfer constant, $C_{T_C} = k_T/k_{cc} = 0.135$, which, in a first approximation, may be expected to be constant over 10°C interval.

Using these values and those derived above for the three reactivity ratios, it is possible to calculate n from equation 23. The results applied to the solution experiments previously described [1], are given in Table 4 and compared with the experimental values and those calculated using the "antepenultimate effect" model. The present theory of the internal transfer reaction also gives a reasonably good account of the copolymerization kinetics.

DISTRIBUTION OF BRANCHES AND SEQUENCES

The method of Ito and Yamashita [10] is followed, according to which any sequence is considered to have a precursor or a successor. It follows that the probability of the existence of a A unit, for instance, P(A), may be written in term of the probability of existence of diads:

$$P(A) = P(AA) + P(AC) = P(AA) + P(CA)$$

from which

$$P(AC) = P(CA)$$

TABLE 4. Experimental and Calculated Vinyl Chloride (C)-Vinyl Acetate (A) Copolymer Composition

x = A/C		33	6.66	2.22	0.95	0.465	0.222	0.112	0.068	0.030	0.023
n = dA/dC	Exp	9.60	2.22	0.86	0.41	0.224	0.133	0.0615	0.039	0.0175	0.0156
	Cal[a]	9.42	2.17	0.81	0.39	0.217	0.115	0.0615	0.039	0.0173	0.0135
	Cal[b]	9.60	2.24	0.91	0.46	0.248	0.125	0.065	0.040	0.0179	0.0141

[a] Calculated according to the antepenultimate effect hypotheses.
[b] Calculated according to the internal transfer effect theory.

It is easy to show that this equation remains valid for the case of branched polymers produced by an internal transfer mechanism: the propagation steps only are considered and the addition of a X unit (A or C) to a B° radical is considered as a CX sequence because one assumes that the internal transfer reaction involves only ACC° or AAC° radicals, both ended by a C unit.

The second statement of Ito and Yamashita, defining the conditional probabilities $p_{xyz} = P(XYZ)/P(XY)$, is used also. The main problem is to derive the correct expression of the conditional probabilities which may eventually contain the transfer probability P_b. The expression of this is

$$P_b = \frac{k_T(AAC^{\circ} + ACC^{\circ})}{k_T(AAC^{\circ} + ACC^{\circ}) + k_{ca}(AAC^{\circ} + ACC^{\circ})A + k_{cc}(AAC^{\circ} + ACC^{\circ})C}$$

$$= \frac{1}{1 + \dfrac{k_{ca}A + k_{cc}C}{k_T}} \qquad (28)$$

Using the kinetic definitions, the conditional probabilities of the propagation steps are

$$p_{ca} = 1 - p_{cc} = \frac{k_{ca}C^{\circ}A + k_{ba}B^{\circ}A}{k_{ca}C^{\circ}A + k_{cc}C^{\circ}C + k_{ba}B^{\circ}A + k_{bc}B^{\circ}C} \qquad (29)$$

$$p_{ac} = 1 - p_{aa} = \frac{k_{ac}A^{\circ}C}{k_{ac}A\ C + k_{aa}A^{\circ}A} \qquad (30)$$

from which

$$n = \frac{P(A)}{P(C)} = \frac{p_{ca}}{p_{ac}} = \frac{(k_{ca}C^{\circ}A + k_{ba}B^{\circ}A)(k_{ac}A^{\circ}C - k_{aa}A^{\circ}A)}{k_{ac}A^{\circ}C(k_{ca}C^{\circ}A + k_{cc}C^{\circ}C + k_{ba}B^{\circ}A + k_{bc}B^{\circ}C)} \qquad (31)$$

Using Eqs. (17) and (19), it is easy to show that Eqs. (31) and (22) are identical.

The conditional probability of a propagation step following a transfer reaction is also needed:

$$p_{bc} = \frac{k_{bc}B^\circ C}{k_{bc}B^\circ C + k_{ba}B^\circ A} \quad \text{and} \quad p_{ba} = \frac{k_{ba}B^\circ A}{k_{ba}B^\circ A + k_{bc}B^\circ C}.$$

Using these six basic conditional probabilities, all the functions of the sequence distribution may be easily derived. It is particularly interesting to calculate the number of branches. The fraction of the A units engaged in the two kinds of branches ACC and AAC are

$$P(\widehat{ACC})/P(A) = P_{ac}P_{cc}P_{b} \tag{32}$$

and

$$P(\widehat{AAC})/P(A) = P_{aa}P_{ac}P_{b} \tag{33}$$

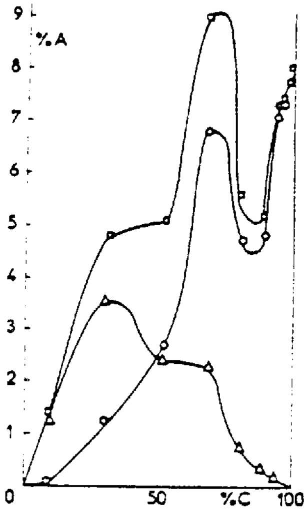


FIG. 6. Per cent of A units engaged in branches [(□) total, (○) ACC branches, (△) AAC branches, vs the per cent of C units in the initial copolymer.

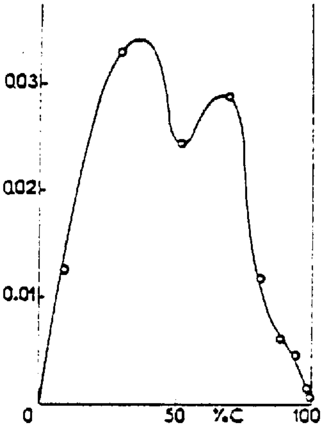


FIG. 7. Probability of existence of branches for solution copolymers as a function of the per cent of C units in the initial copolymer.

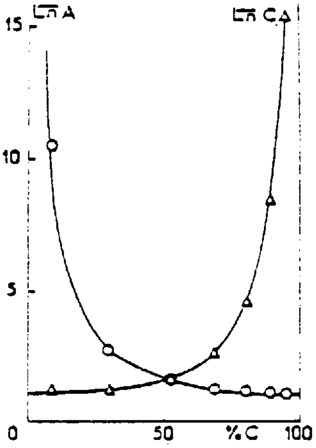


FIG. 8. Number-average length of A sequences (○) or C sequences (△) vs the per cent of C units in the initial copolymer.

Figure 6 gives a plot of these two expressions and of their sum. The rather complex shapes of the curves arise from the fact that the three conditional probabilities involved in each equation do not vary in the same manner with the composition of the copolymers. For instance, when $x \to 0$, P_{cc} and P_{ac} tend to 1, $p_{aa} \to 0$, and $p_b \to 1/(1 + k_{ccC}/k_T)$ so that the expression of Eq. (32) tends toward a finite limit while the other kind of branch tends to disappear. The actual probability of existence of a branch (both kinds) is illustrated in Fig. 7, calculated for the condition of solution polymerization [1]. For the same conditions, Fig. 8 gives the number-average length of the sequences of nonbranched units. The expressions used to calculate them are more complex than the simple expression in the case of a linear copolymer when one has $\overline{L_n}(A) = 1/P_{ac}$ and $\overline{L_n}(C) = 1/P_{ca}$. In the present case

$$L_n(A) = \frac{1}{P_{ac}} \left(\frac{1 - p_b p_{ac}(p_{cc} + 2\, p_{aa})}{1 - p_b p_{ac}(p_{cc} + p_{aa})} \right)$$

and

$$\overline{L_n}(C) = \frac{1}{P_{ca}} \left(\frac{1 - p_b p_{ca}(p_{aa} + 2\, p_{cc})}{1 - p_b p_{ba}(p_{aa} \bullet p_{cc})} \right)$$

The branching may also introduce some new features, so the probabilities of triads containing branches are not reversible and, for instance,

$$P(ABC) = P(A)p_{aa}(p_{ac}p_{cc}p_b)p_{bc} \neq P(CBA) = P(A)p_{ac}(p_{ac}p_{cc}p_b)p_{ba}$$

DISCUSSION

The above results clearly show that an internal transfer reaction involving a C-ended radical and the tertiary hydrogen atom of a A unit actually occurs. A kinetic scheme including that reaction and excluding penultimate effects gives a reasonably good account of the kinetic results. Other transfer reactions which cannot be studied from the NMR spectra of the copolymer possibly also occur and might involve A- or C-ended radicals and A or C units. However, they are probably quite infrequent compared with the reaction assumed here. The possibility of short branches in the homopolymer has also been considered but as a minor irregular structure.

It is interesting to note that the internal transfer reaction is concentration dependent because there is competition for the ACC°

or AAC° radicals between the transfer reaction and the two propagation reactions. Transfer is expected to be more frequent when the polymerization is carried out in dilute solution. We have some data to support this theory but they are not accurate enough to be published here.

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Accepted by editor June 9, 1972
Received for publication June 22, 1972