

Anomalous addition in ethylene-vinyl acetate copolymerization

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ON ANOMALOUS ADDITION IN ETHYLENE-VINYL ACETATE COPOLYMERIZATION

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Abstract—Kinetic and spectroscopic methods for revealing anomalous vinyl acetate-ethylene additions are compared. An expanded copolymer equation is derived. According to this model description, kinetic measurements recording monomer consumption are very insensitive to anomalous addition. It is shown that both i.r. and NMR measurements may be used as methods of determining anomalous additions: the results agree satisfactorily. These results indicate that the fraction of vinyl acetate anomalously adding to an ethyl radical chain-end increases as the ethylene content of the copolymer increases, a finding which may be explained by penultimate effects in anomalous addition.

Homopolymerization of vinyl monomers gives polymers with 98–100 per cent “head-to-tail” structure because of the greater thermodynamic advantage of the corresponding propagation step. According to Flory and Leutner [1] the fraction of “head-to-head” addition at 62° can be calculated as 1.5 per cent of the total number of additions in the case of vinyl acetate. In copolymerization, conditions are more favourable to forming “head-to-head” units if, e.g. ethylene is involved, since steric inhibitions and polarity factors restricting the possibility of anomalous addition in homopolymerization, are partly absent.

Anomalous addition reactions in high-pressure ethylene-vinyl acetate copolymerization have been considered by Lyubetzky *et al.* [2,3]. However, in their derivation of an expanded copolymer equation taking into account anomalous additions, some dubious assumptions and approximations were made and, unfortunately, the resulting equation is not quite correct in the published form. So it seems worthwhile to consider an amended model description, and to discuss the possibility of revealing anomalous addition from kinetic and spectroscopic investigations.

EXTENSION OF THE MODEL FOR FREE-RADICAL VINYL COPOLYMERIZATION

The occurrence of anomalous additions can generally be considered as a special case of three-component terpolymerization, where the third component (c) is the anomalously added second component (b). Considering all terpolymer chains, four possibilities seem to exist in which an a sequence can be bounded:

ba a ab
 ba a ac
 ca a ab
 ca a ac

If only propagation steps are considered (which means high molecular weight and steady state for the radicals), it can be seen that the number of sequence-starting transitions equals the number of sequence-ending transitions. An a sequence can be started by

either a ba or a ca transition and be ended by an ab or an ac transition.

For instance, by definition, p_{ba} is equal to the probability of monomer a adding to radical b, which is equivalent to saying that p_{ba} is the fraction of the b units present in the terpolymer and followed by an a unit. If A, B and C are the absolute amounts of a, b and c present in the terpolymer, respectively, the absolute amount of for example ba transitions is Bp_{ba} and consequently:

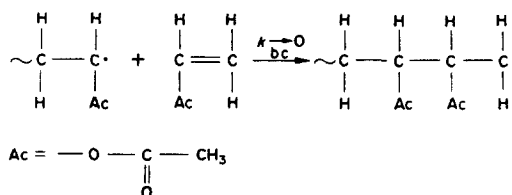
$$Bp_{ba} + Cp_{ca} = Ap_{ab} + Ap_{ac} \text{ for a sequences. (1)}$$

similarly

$$Ap_{ab} + Cp_{cb} = Bp_{ba} + Bp_{bc} \text{ for b sequences (2)}$$

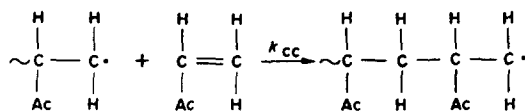
and

$$Ap_{ac} + Bp_{bc} = Cp_{ca} + Cp_{cb} \text{ for c sequences. (3)}$$



Lyubetzky *et al.* [2,3] made the following assumptions (expressed in the nomenclature used here) for ethylene (a), vinyl acetate “head-to-tail” (b), vinyl acetate “head-to-head” (c), $p_{bc} = 0$, and $p_{cc} = 0$ or $p_{ca} + p_{cb} = 1$. $p_{bc} = 0$ means that a vinyl acetate chain end will not add anomalously a vinyl acetate unit. This may seem a reasonable assumption, since according to Flory *et al.* [1] only 1.5% of the propagation steps in homopolymerization of vinyl acetate at 62° lead to anomalous addition. Goff *et al.* [4] found that an increase of pressure from atmospheric to 6000 kgf/cm² during homopolymerization of vinyl acetate at 40° leads to a relative increase of 22% in anomalous “head-to-head” additions. But even then the assumption $p_{bc} = 0$ seems quite acceptable. On the other hand, $p_{cc} = 0$ means that anomalous addition of vinyl acetate will never be followed by another anomalous addition. At present no reasonable grounds are available to justify this statement, the more so as this addition is not restricted by either polarity factors or

steric hindrance. For this reason only the assumption $p_{bc} = 0$ will be made in the following derivation.



From Eqns. (1)-(3), it can be shown that

$$\frac{A}{B + C} = \frac{p_{ba}(p_{ca} + p_{cb})}{p_{ab}(p_{ca} + p_{cb}) + p_{ac}(p_{cb} + p_{ba})} \quad (4)$$

After the definition for p_{ba} (in which k = reaction rate constant and n = number of moles monomer in the feed):

$$p_{ba} = \frac{k_{ba} n_a}{k_{ba} n_a + k_{bb} n_b + k_{bc} n_c}$$

and analogous expressions for p_{ca} , p_{cb} , p_{ab} and p_{ac} , Eqn. (4) takes the form:

$$\frac{dn_a}{dn_b} = F \frac{r_a + \frac{1}{F}(m + 1)}{(r_b/F) \left(1 + \frac{mr_c}{F + r_c}\right) + 1 + m \left(1 + \frac{r_c + r'_c}{F + r_c}\right)} \quad (5)$$

where

$$\begin{array}{ll} \frac{dn_a}{dn_b} = \frac{A}{B + C} & \frac{k_{cc}}{k_{ca}} = r'_c \\ \frac{k_{aa}}{k_{ab}} = r_a & \frac{k_{ac}}{k_{ab}} = m \\ \frac{k_{bb}}{k_{ba}} = r_b & n_b = n_c \\ \frac{k_{cb}}{k_{ca}} = r_c & \frac{n_a}{n_b} = F \end{array}$$

When $m = 0$, Eqn. (5) reduces to the conventional copolymer equation [5,6].

DISCUSSION

As in Eqn. (5) both numerator and denominator increase with increasing number of anomalous additions, it can be predicted that change in the rates of disappearance of the monomers will be rather insensitive to changes in the occurrence of anomalous additions; this conclusion has been confirmed by simulative calculations.

Earlier investigations [7] on the kinetics of ethylene-vinyl acetate copolymerization at low pressure (35 atm) indicate that the experimental data are precisely consistent with the usual Mayo-Alfrey

model [5,6]. This means that anomalous additions do not disturb the model fitting within the narrow limits imposed by the experimental error. The latter does not mean, however, that anomalous addition does not occur in these copolymers, but, from kinetic measurements, it cannot be decided whether anomalous addition occurs either only rarely or more often with a rate constant only slightly different from that of the normal addition. Inasmuch as the occurrence of anomalously adding vinyl acetate to ethyl radical chain ends has a small effect in kinetic measurements recording monomer consumption [8], it is not surprising that those measurements, though very precise, do not reveal this effect.

Since the presence of anomalous addition shows up unequivocally in e.g. i.r. and NMR spectra, we have resorted to these techniques.

EXPERIMENTAL

The copolymers were prepared at 62° and 35 atm in *tert*-butylalcohol with α , α' azodiisobutyronitrile. The relevant samples were collected before 15% conversion was reached. Details are given elsewhere [7].

Infra-red spectroscopy

Infra-red measurements were carried out by a method partly analogous to that described by Lyubetzky *et al.* [2,3], based on determination of $-(\text{CH}_2)_2-$ sequences which are characteristic of anomalous addition and of $-(\text{CH}_2)_1-$ and $-(\text{CH}_2)_3-$ groups which indicate normal addition. The following modifications were made.

In the calculation of the concentrations of the $-(\text{CH}_2)_1-$, $-(\text{CH}_2)_2-$ and $-(\text{CH}_2)_3-$ groups, the "molar" absorptivities of these groups have been taken into account. An estimation of the relevant "molar" absorptivities has been derived from values reported by McMurry and Thornton [9] for methylene sequences in paraffinic hydrocarbons as well as from our own measurements on model compounds (see Table 1).

In addition, Lyubetzky's factor λ , representing the fraction of $-(\text{CH}_2)_2-$ sequences formed by "head-to-head" addition has been calculated according to the relation $\lambda = \bar{x}/(\bar{x} + 1)$. The number average sequence length of ethylene sequences (\bar{x}) has been calculated from the kinetic data [7]. This estimation of λ holds under the following conditions: (1) any anomalous vinyl acetate to ethylene addition will be followed either directly, or after a sequence of anomalous vinyl acetate to vinyl acetate additions, by a normal vinyl acetate addition; and (2) the number average sequence length of vinyl acetate sequences ≥ 2 .

The first condition is probably met but cannot be easily verified. The second condition is completely satisfied in the present case.

For the various samples, the percentage of anomalous vinyl acetate additions to ethyl radical chain-ends has been computed according to the equation:

$$\% \text{ anomalous addition} = \lambda \left(\frac{A_{743 \epsilon_2}}{A_{797 \epsilon_1} + A_{743 \epsilon_2} + A_{725 \epsilon_3}} \right) \times 100\%$$

Table 1. Rocking deformation vibrations of methylene sequences in ethylene-vinyl acetate copolymers

Sequence	Band cm^{-1}	"Molar" absorptivity ϵ $\text{mole}^{-1} \text{cm}^{-1}$
$-(\text{CH}_2)_1-$	797	$\epsilon_1 = 6.5$
$-(\text{CH}_2)_2-$	743	$\epsilon_2 = 9.0$
$-(\text{CH}_2)_3-$	725	$\epsilon_3 = 10.5$

Table 2. Anomalous addition of vinyl acetate to ethyl radical chain-ends related to copolymer composition

Mole % ethylene in copolymer	λ	% of anomalous vinylacetate additions to ethyl radical chain ends	
		IR	NMR
9.5	0.53	3.9	4.6
10.0	0.53	4.2	4.4
11.8	0.53	5.6	-
16.2	0.54	7.0	8.1
31.3	0.60	10.2	12.0
33.7	0.61	10.8	12.0
43.3	0.66	14.8	13.2

The absorbances (A) were measured from i.r. spectra of copolymer films (film thickness approx. 0.1 mm) recorded with an Hitachi-EPI G04 spectrophotometer. A typical spectrum is shown in Fig. 1.

The results of the measurements are shown in Table 2.

NMR measurements

In order to provide further evidence, NMR analysis has been applied. The sample solutions were prepared to contain 10 wt % of copolymer in chloroform. Tetramethylsilane was added as an internal reference. The spectra were recorded with a Varian HA 100 MHz spectrometer using the double resonance technique which permits spin-spin decoupling of the methylene and methine proton spectra. In addition, the integrals were recorded. A typical spectrum is shown in Fig. 2.

The percentage of anomalous vinyl acetate additions to ethyl radical chain-ends has been calculated according to:

$$\% \text{ anomalous addition} = \lambda \left(\frac{S_b}{2S_a + S_b + S_c} \right) \times 100\%$$

where S_a , S_b , and S_c are the areas of the relevant peaks (see legend Fig. 2). The results are listed in Table 2.

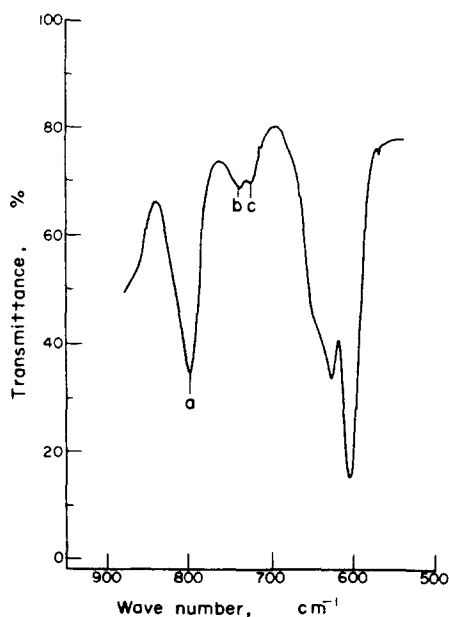


Fig. 1. Infra-red spectrum of an ethylene-vinyl acetate copolymer (11.8 mole % ethylene). Sample thickness, 0.07 mm. 797 cm^{-1} , $-(\text{CH}_2)_1-$, peak a; 743 cm^{-1} , $-(\text{CH}_2)_2-$, peak b; 725 cm^{-1} , $-(\text{CH}_2)_3-$, peak c.

RESULTS AND DISCUSSION

While precise kinetic measurements [8] do not indicate the occurrence of anomalous additions in ethylene-vinyl acetate copolymerization, their presence can be revealed by i.r. as well as NMR analysis.

Although the results of the two techniques agree satisfactorily, we consider the NMR method to be the more reliable, because the proton signals are directly proportional to the proton concentrations whereas the "molar" absorptivities required for i.r. measurements will impair the accuracy. The order of magnitude of the percentage of anomalous addition

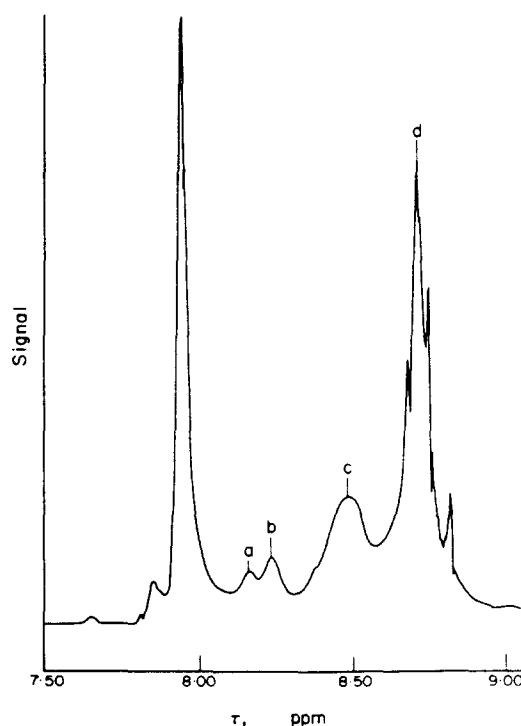
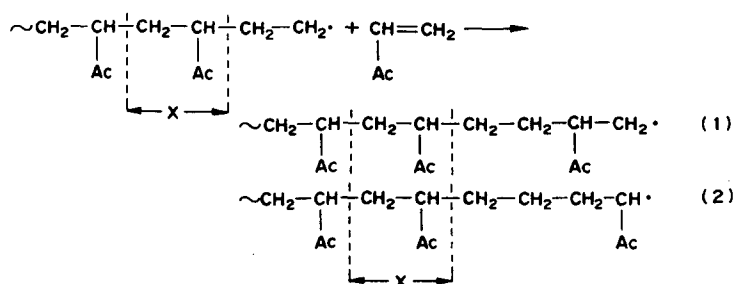


Fig. 2. Double resonance NMR spectrum (100 MHz) of an ethylene-vinyl acetate copolymer (43.3 mole % ethylene). Tetramethylsilane as internal standard. $\tau = 7.95$, $\text{CH}_3\text{COO}-$; $\tau = 8.15$, $-\text{CHAc}-\text{CH}_2-\text{CHAc}-$, peak a: $\tau = 8.20$, $-\text{CHAc}-\text{CH}_2-\text{CH}_2-\text{CHAc}-$, peak b: $\tau = 8.50$, $-\text{CHAc}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CHAc}-$, peak c: $\tau = 8.70$, $-\text{CHAc}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CHAc}-$, including $-\text{CHAc}-\text{CH}_2-(\text{CH}_2)_n-\text{CH}_2-\text{CHAc}-$, peak d.



is confirmed by an estimation of 15% by Lyubetzky *et al.* [2,3].

It is apparent from the results of the structural investigations (see Table 2) that the percentage of anomalous vinyl acetate to ethylene additions increases from 5 to 13% as the amount of ethylene in the copolymer increases from 10 to 43 mole %. This significant phenomenon leads to the conclusion that the anomalous addition of vinyl acetate to an ethyl radical chain-end is statistically less advantageous when the penultimate unit of the growing chain is vinyl acetate as compared with ethylene.

The minimum "distance" between two acetate side-groups, resulting from an anomalous vinyl acetate addition to an ethyl radical chain-end [eqn. (6)], is two methylene groups. In the case of a normal addition of vinyl acetate to an ethyl radical chain end [Eqn. (7)], this minimum "distance" is three methylene groups. Therefore, penultimate influences on polarity factors and steric hindrance will play a greater part in the anomalous addition according to [Eqn. (6)] than in the normal addition given in [Eqn. (7)].

Consequently, the anomalous addition [Eqn. (6)] will be more sensitive to replacement of residue X by an ethylene unit than the normal addition [Eqn. (7)]. This is in agreement with the present results.

Finally, it should be emphasized that only anomalous vinyl acetate to ethylene addition can be revealed by the present techniques. Once a polymer chain has

been formed, any possible sequences of anomalously added vinyl acetate units can basically not be distinguished from normal sequences. Only knowledge of the complete distribution of units along the polymer chain would provide sufficient information to solve completely the general problem of anomalous addition. These considerations suggest that all of the evidence is not yet available on the occurrence of anomalous addition even in apparently normal vinyl homopolymerization.

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