

Copolymerization of Ethylene with Vinyl Acetate.

I. Effect of Polymerization Temperature on Degree of Branching*

M. J. WISOTSKY, A. E. KOBER, and I. A. ZLOCHOWER,
*Esso Research and Engineering Company, Linden,
New Jersey 07036*

Synopsis

The degree of branching of a series of ethylene-vinyl acetate copolymers was found to be strongly dependent upon polymerization temperature. The copolymers were prepared by free-radical polymerization and had low molecular weights and molar ratios of ethylene:vinyl acetate greater than 3:1. Nuclear magnetic resonance and infrared studies showed that copolymers prepared at 150°C were highly branched and had little crystallinity. Branches were mainly alkyl groups on the polymethylene backbone segments. There was no evidence of δ -acetoxyalkyl branches. Long branches originating by intermolecular H abstraction from the acetylmethyl groups were also expected but could not be detected. These results were consistent with an intramolecular "backbiting" mechanism similar to that found in ethylene homopolymerizations. There was little or no participation by the vinyl acetate moiety in the branching scheme. Copolymers prepared at about 90°C had very few long or short branches and were more crystalline. Copolymers prepared between these temperatures had intermediate degrees of branching and crystallinity.

INTRODUCTION

Degree of branching is an important factor affecting polymer properties.¹ For free-radical copolymerizations such as ethylene-vinyl acetate, the activation energy for chain branching is greater than that for chain propagation, and branching is expected to increase with temperature.^{2,3}

In the polymers described here, the molar ratios ranged from approximately 3:1 to 7:1 ethylene:vinyl acetate. Since the polymers consisted mostly of ethylene units, it was expected that the type of branching should be similar to that found in ethylene polymerizations. Branch formation is depicted in Figure 1. For ethylene homopolymerizations, most chain branching arises from an intramolecular chain transfer mechanism called "backbiting." This mechanism operates via an intermediate six-membered

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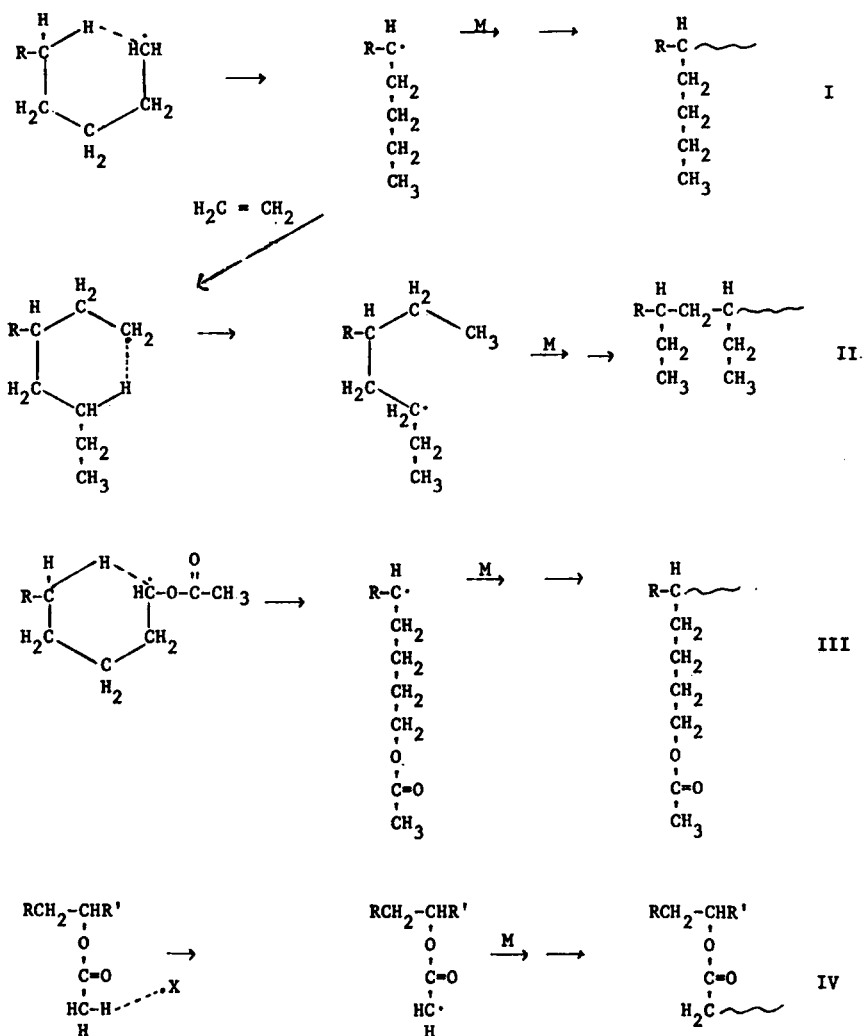


Fig. 1. Branch formation in poly(ethylene-vinyl acetate).

ring and produces butyl branches (I in Fig. 1).⁴ Addition of an ethylene unit followed by another intramolecular chain transfer results in ethyl branches (II).^{5,6} Intermolecular H abstractions lead to long polyethylene branches off the main backbone.⁷

In ethylene-vinyl acetate copolymerizations, the "backbiting" mechanism should lead to a majority of alkyl branches with a possibility of some δ -acetoxyalkyl branches when the terminal radical is on a vinyl acetate group (III). Intermolecular chain transfer should occur most readily through the acetylmethyl H atoms resulting in long branches with the same composition as the polymer backbone (IV).

DISCUSSION

A series of ethylene-vinyl acetate copolymers was prepared at temperatures from 80° to 150°C. The polymers exhibited large differences in nuclear magnetic resonance and infrared properties consistent with different degrees of branching.

Proton Nuclear Magnetic Resonance (NMR)

Quantitative estimates of the degree of branching in a series of ethylene-vinyl acetate copolymers prepared at different temperatures were obtained from NMR spectra. The number of alkylmethyl groups in the copolymer is indicative of branching in the polymethylene backbone segments (I and II). These were calculated from the alkylmethyl proton resonance (0.09 ppm/CCL₄) using the acetate methyl proton resonance (1.95 ppm/CCL₄) as reference. The data were adjusted for differences in polymer molecular weight by expressing the result as number of alkylmethyls/1000 mol. wt. or CH₃/1000 mol. wt. Copolymers prepared at the same temperature but with different solvents and/or initiators, and having different ester contents and/or molecular weights, all gave the same number of CH₃/1000 mol. wt. This is a strong indication that the degree of branching is governed predominantly by polymerization temperature and is not affected by method of preparation. Data are given in Table I and are summarized in Figure 2.

Copolymers prepared at 110°C or lower contain about 1.3 CH₃/1000 mol. wt. or approximately one alkyl group for every 20 ethylene backbone units. These copolymers are essentially linear. At 125°C there are 1.9 CH₃/1000 mol. wt., and at 150°C the figure is 4.1 CH₃/1000 mol. wt. The latter copolymers contain about one alkyl group for every four ethylene units and are thus highly branched. This figure is approximate, since no attempt was made to distinguish between the butyl and ethyl branches of I and II.

TABLE I
Effect of Temperature on the Degree of Branching in Poly(Ethylene-Vinyl Acetate)

Sample	Polymerization temp., °C	VAc, wt. %	VPO, mol. wt.	Number of	
				$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{C}-/\text{CH}_3 \end{array}$	Number of CH ₃ /1000 mol. wt.
A	80	46	1860	3.7	1.4
B	85	33	2526	2.8	1.4
C	105	38	2160	3.6	1.2
D	105	38	2200	3.0	1.4
E	105	39	2000	3.5	1.3
F	105	38	2940	3.5	1.3
G	125	32	2220	2.0	1.9
H	145	30	1452	1.2	2.9
I	150	32	3832	0.9	4.1

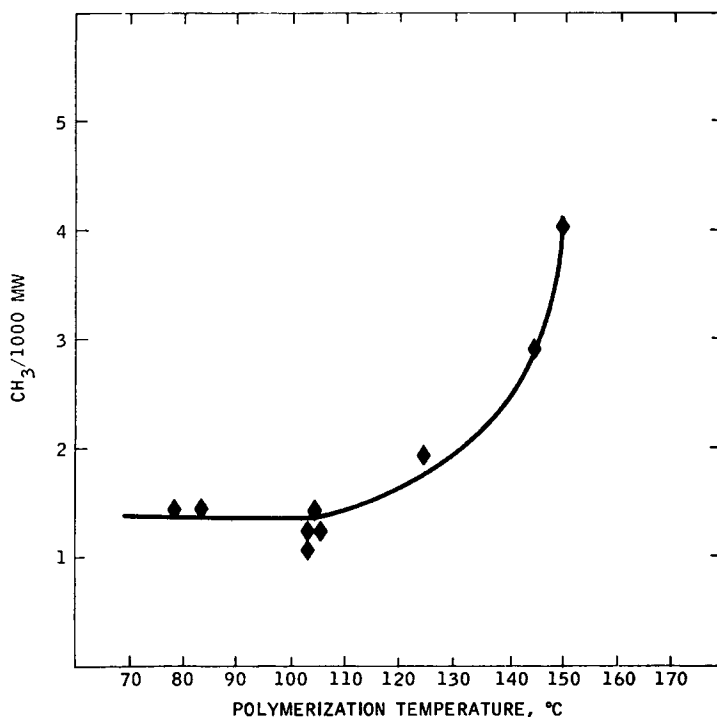


Fig. 2. Effect of polymerization temperature on branching of poly(ethylene-vinyl acetate).

No absorption was observed in the 4.2-ppm region which would be characteristic⁸ of $-\text{CH}_2\text{O}$ protons such as those in δ -acetoxyalkyl groups (III). This indicates little or no "backbiting" by propagating vinyl acetate radicals.

Also, no absorption was observed at about 2.1 ppm characteristic of the $-\text{CH}_2\text{CO}-$ protons in the long branches of structure IV. The absence of appreciable branching off the acetyl methyl group was also indicated by GLPC analysis of acids recovered from hydrolyzed copolymer. The chromatograms exhibited only a single peak corresponding to acetic acid. Also reacylation of the polymer gave spectra identical with those of the original. These results indicate the absence of branching on the acetate methyl group.

Infrared

Infrared spectra of copolymers prepared at 85°, 125°, and 150°C were examined in the 720–730 cm^{-1} region. The polymers exhibited strong absorption at 720 cm^{-1} , which is characteristic of the polymethylene $-(\text{CH}_2)_x-$ bending vibration. In addition, the polymer prepared at 85°C gave an auxiliary peak at about 730 cm^{-1} , which is indicative of crystallinity

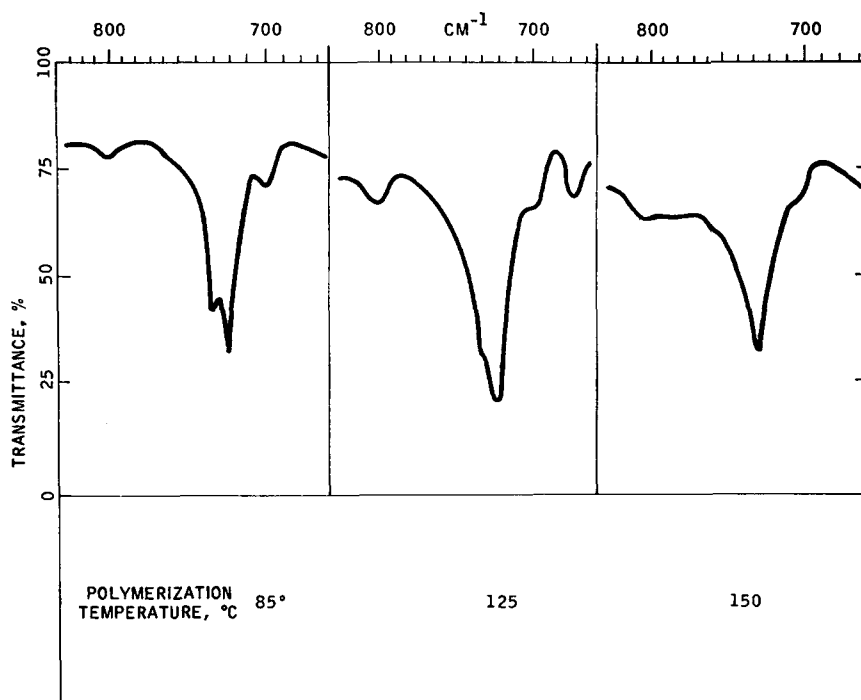


Fig. 3. Effect of polymerization temperature on infrared spectra of poly(ethylene-vinyl acetate).

or linearity.⁹ This peak was absent in the 150°C polymer, which is consistent with a highly branched amorphous structure and appeared as a shoulder in the 125°C polymer spectrum. The infrared spectra are illustrated in Figure 3.

EXPERIMENTAL

Copolymers were prepared by free-radical solution and emulsion polymerization in a stirred autoclave at constant temperature and pressure. Copolymer number-average molecular weights were obtained by vapor pressure osmometry and vinyl acetate contents by elemental analysis and saponification number. Copolymer compositions were assumed to be random since the reactivity ratios of ethylene and vinyl acetate are both unity.¹⁰

Nuclear magnetic resonance spectra were obtained on solutions of copolymer in benzene and/or chlorinated hydrocarbons using Varian A-60 or HA-100 spectrometers.

Samples of copolymer were saponified and extracted with hot water. Acids recovered from the aqueous extracts were subjected to GLPC analysis on a silicone column. Hydrolyzed copolymers were reacylated with acetic anhydride in pyridine.

Infrared spectra were obtained on thin samples of polymer using a Perkin-Elmer Infracord spectrophotometer.

CONCLUSIONS

The results of these studies indicate that poly(ethylene-vinyl acetate) undergoes chain branching reactions similar to those of polyethylene. There is very little participation by the vinyl acetate moiety. Copolymers prepared at 150°C have highly branched polymethylene backbone segments, while copolymers prepared at 100°C or lower are essentially linear. Copolymers prepared between these temperatures have intermediate degrees of branching.

References

1. M. Saito, H. Tada, and Y. Kosaka, *J. Polym. Sci. A-1*, **8**, 2555 (1970).
2. S. Machi, T. Sakai, T. Tamura, M. Gotoda, and T. Kagia, *Polymer Letters*, **3**, 709 (1965).
3. S. Machi, S. Kise, M. Hagiwara, and T. Kagia, *J. Polym. Sci. A-1*, **5**, 3115 (1967).
4. M. J. Roedel, *J. Amer. Chem. Soc.*, **75**, 6110 (1953).
5. A. H. Willbourn, *J. Polym. Sci.*, **34**, 569 (1959).
6. G. A. Tirpak, *Polymer Letters*, **4**, 111 (1966).
7. P. J. Flory, *J. Amer. Chem. Soc.*, **59**, 241 (1957).
8. R. M. Silverstein and G. C. Bassler, *Spectrometric Identification of Organic Compounds*, New York, 1963.
9. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., Wiley, New York, 1958.
10. R. A. Terteryan, E. E. Brando, and A. I. Dintsès, *Usp. Khim.*, **34**, 666 (1965).

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