

^{13}C n.m.r. study of solvation mechanisms in the radiation-induced polymerization of vinyl ethers

Alain Deffieux and Franck Subira

Laboratoire de Chimie Macromoléculaire, Université Pierre et Marie Curie, 4, place Jussieu, Tour 44, 75230 Paris Cedex 05, France

and Vivian T. Stannett

Department of Chemical Engineering, North Carolina State University, Raleigh, N.C. 27650, USA

(Received 5 October 1983)

A ^{13}C n.m.r. study of the microstructure of ethyl vinyl ether (EVE) and isopropyl vinyl ether (IPVE) polymers prepared under various experimental conditions and using chemical or γ -ray initiation has been made. Long stereo-sequence assignments were conducted for poly EVE allowing determination of the configurational statistics of propagation in the radiation-induced polymerization of EVE in low polar solvents. Stereo-sequence intensities are found in good agreement with the Markovian model. The results are considered as further support for the occurrence of a specific interaction between the growing active centres and the polymer chains. In the case of IPVE polymers much more important overlappings of the resonance patterns are observed thus preventing any similar detailed study.

(Keywords: cationic polymerization; radiation-induced polymerization; poly(ethyl vinyl ether); poly(isopropyl vinyl ether); ^{13}C nuclear magnetic resonance; solvation)

INTRODUCTION

The radiation-induced polymerization of vinyl ethers is known to proceed, under extremely dry conditions, through an unpaired cationic mechanism¹⁻² and the kinetics of the propagation reactions of ethyl (EVE) and isopropyl vinyl ethers (IPVE) have been studied in detail in different media ranging from bulk hydrocarbons and ethers to nitromethane³⁻⁶. A predominant effect of solvation on the reactivity of the unpaired propagating cations has been proposed to explain the overall kinetic results. Briefly, in the polymerization of EVE in solvents of low polarity^{3,5} reactivities have been interpreted by a predominant solvation of the free propagating cations by the polymer chains themselves, whereas, in methylene dichloride⁴ and in nitromethane, the growing poly EVE chain ends appear to be solvated mainly by the solvent molecules. With the IPVE monomer the much higher reactivity observed in media of low polarity was attributed to a drastic reduction of the intramolecular solvation of the growing polymer chain ends due to the bulkiness of the isopropyl side groups⁶. Further arguments supporting these solvation effects have been found in the determination and analysis of reactivity ratios and rates of consumption of EVE and IPVE monomers in a study of their radiation-induced bulk copolymerization⁷: it was observed that the presence of EVE units in the copolymer chains led to a drastic decrease in reactivity for the IPVE growing ends again supporting the assumption of a strong deactivating solvation effect between incorporated EVE units and growing cations.

Another approach to these solvation mechanisms has been developed very recently in our laboratories using ^{13}C n.m.r. to study the microstructure of the poly(vinyl ethers). This paper deals with the ^{13}C n.m.r. analysis of both polyEVE and polyIPVE. An assignment of the configurational stereo-sequences of polyEVE up to tetrads and pentads is proposed and the statistic aspects of monomer propagation for γ -ray polymerizations in low polarity solvents is discussed.

EXPERIMENTAL

Material

The purification and drying of monomers and solvents using high vacuum techniques have already been reported^{4,5,8}. Boron trifluoride etherate (BF_3OEt_2) (Aldrich) was distilled twice *in vacuo* and stored in calibrated phials connected with teflon stopcocks.

Polymerizations

All the experiments were carried out under rigorously dry conditions under high vacuum.

Chemically-induced polymerization. Solutions of the initiator (25 ml, 10^{-3} M) were cooled and then thermostated in the reactor before the monomer (1 ml) was rapidly introduced. The mixture was allowed to react for 30 min. Polymerizations were halted by adding a small amount of methanol. The polymers were separated by pouring the reaction medium into a large excess of

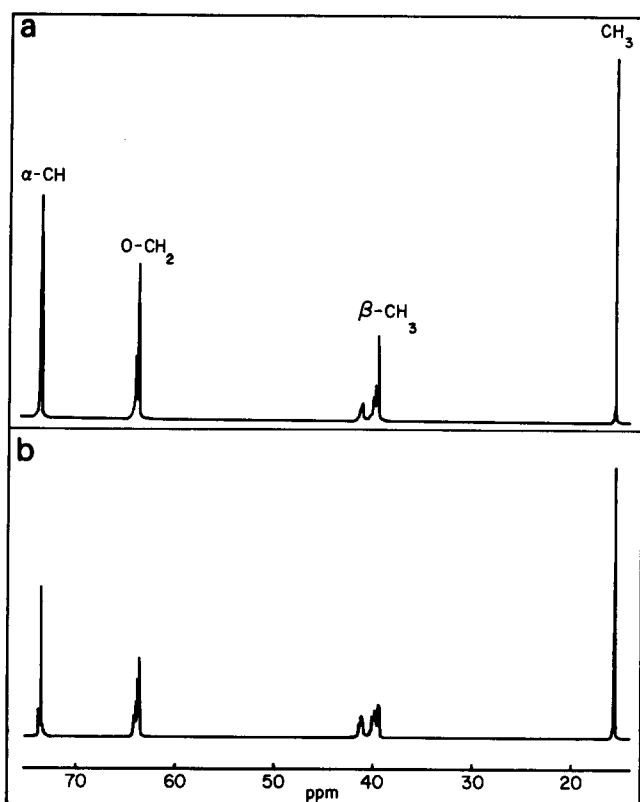


Figure 1 62.89 MHz ^{13}C n.m.r. spectra of polyEVE. (a) PolyEVE 1 prepared with BF_3OEt_2 in toluene at -78°C . (b) PolyEVE 2 prepared with BF_3OEt_2 in CH_2Cl_2 at -78°C . Spectra in CDCl_3 , at 20°C (10 000 transients)

methanol. Complete conversions were generally observed.

Radiation-induced polymerization. These were carried out in sealed ampoules using a ^{60}Co source and under controlled temperature, as previously described³. After an appropriate irradiation time the solvent and residual monomers were completely removed by evaporation under vacuum.

N.m.r. measurements

$^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra were recorded at room temperature, at 62, 89 MHz on a Bruker instrument, on CDCl_3 polymer solutions (10% w/v).

Relative peak intensities of overlapping patterns were determined by means of a curve resolution program assuming linear combinations of Lorentzian and Gaussian peak shapes. The fit between calculated and experimental envelopes was obtained by varying the number of the peaks and their location, intensity and width. Best fitting was generally observed when using a 20 to 30% Gaussian shape contribution.

RESULTS AND DISCUSSION

Poly(ethyl vinyl ether)

Stereo-sequences assignment. The assignment and the

chemical shifts corresponding to the methine (>CH),

ethoxymethylene (O-CH_2), β -methylene ($\beta\text{-CH}_2$) and methyl (CH_3) carbons of polyEVE have already been reported by Matsuzaki and coworkers⁹. These authors

proposed an assignment for the diads and triads of the respective $\beta\text{-CH}_2$ and -O-CH_2 resonances.

To observe and assign the resonances of longer stereo-sequences we used high field instrument and poly(ethyl vinyl ethers) of various tacticities which had been prepared in toluene (PEVE 1) and in methylene dichloride (PEVE 2) using BF_2OEt_2 initiators. The 62.89 MHz ^{13}C n.m.r. spectra are shown in Figure 1. The expanded spectra of the side methylene and β -methylene carbons are given in Figure 2.

They clearly show resolved patterns corresponding, respectively, to pentad and tetrad (partly split into hexads) sequences. An attempt to assign these peaks to specific configurations was carried out assuming that the propagation steps could be expressed either by a Bernoulli or first order Markov trial. The corresponding fraction of the tetrad and pentad sequences were calculated from the diad or the relative diad to triad intensities and compared with the peak areas determined by curve resolution of the experimental spectra. Each pentad peak was not conclusively assigned because of the very small differences in chemical shift and only six of the ten pentad peaks were distinguishable. After a comparison between the observed and the calculated peak intensities, the stereo-sequences were tentatively assigned as shown in Table 1. Correct agreement is observed for both samples when first order Markovian statistics are applied for the cationic polymerization of EVE with BF_3OEt_2 initiators. A chain end cyclic structure for the polymerization of vinyl ethers in solvents of low solvating power has been suggested^{10,11} to explain the formation of the isotactic polymer but the stereoregulating influence of the associated counterion has also been postulated¹¹. Both hypotheses may be considered to account for the first order Markovian statistics. Thus in chemical initiation there is no method, as yet, of deciding which of these two effects predominates.

Analysis of polyEVE prepared under γ irradiation. Compared with the chemically-induced

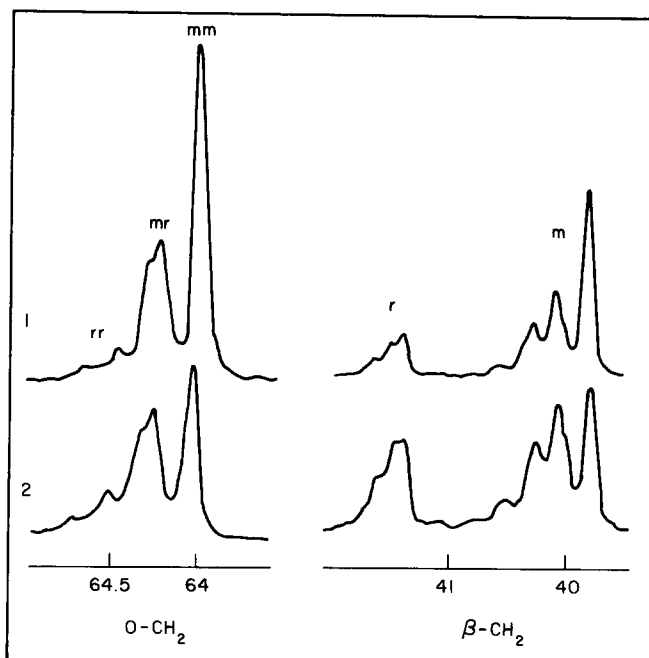
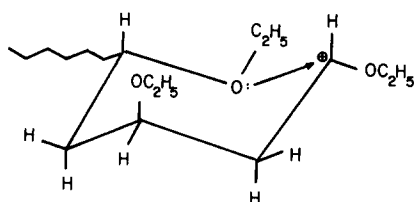


Figure 2 Expanded spectra of the ethoxy methylene (O-CH_2) and β -methylene ($\beta\text{-CH}_2$) of polyEVE 1 and polyEVE 2

Table 1 Observed and first-order Markov calculated proportions of configurational sequences in polyEVE

Sequences	PolyEVE-1		PolyEVE-2	
	Observed	Calculated (Pr/m = 0.86 Pm/r = 0.26)	Observed	Calculated (Pr/m = 0.86 Pm/r = 0.44)
<i>diads</i>	(m)	0.79	0.67	
	(r)	0.21	0.33	
<i>triads</i>	(mm)	0.57	0.36	
	(mr)	0.40	0.57	
	(rr)	0.03	0.07	
<i>tetrads</i>	(mmm)	0.41	0.22	0.20
	(mmr)	0.33	0.33	0.32
	(rmr)	0.05	0.13	0.13
	(mrm)	0.15	0.20	0.23
	(mrr)	0.06	0.12	0.11
	(rrr)	0.00	0.01	0.01
<i>pentads</i>	(mm)	0.57	0.36	0.36
	(mmrm)	0.23	0.25	0.26
	(rmm)	0.12	0.20	0.20
	(rmrr)	0.00	0.03	0.05
	(mmrr)	0.04	0.07	0.06
	(rr)	0.03	0.07	0.07

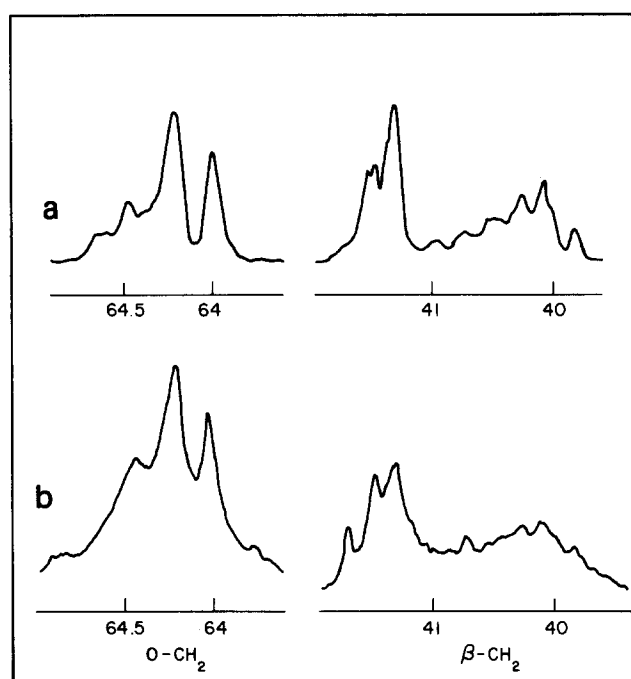
PolyEVE 1 polymerized with BF_3OEt_2 in toluene at -78°C
 PolyEVE 2 polymerized with BF_3OEt_2 in CH_2Cl_2 at -78°C


Figure 3 Chelated polyEVE chain end postulated in the radiation induced polymerization of EVE in low polar solvents

polymerization, the absence of ion pairs is an interesting and simplifying feature of the radiation-induced polymerizations. In the absence of any specific interaction with their surroundings free cations are not represented as having any particular stereochemistry and the statistics of the configurational enchainment of monomer molecules in the building up of a polymer chain are expected to follow the simple Bernoulli trial¹². The occurrence of a Bernoullian process has already been checked in the radiation-induced cationic polymerization of styrene¹³. In the case of the vinyl ethers the occurrence of a specific interaction between the growing active centres and the polymer chain themselves has been postulated to exist in solvents of low polarity³⁻⁵: a ring structure for the polymer growing ends, represented in *Figure 3*, has been proposed.

Taking into consideration the occurrence of such a specific solvation process for the growing ends, we anticipated that the determination of the configurational statistic of the monomer incorporation might afford some structural information concerning the unpaired propagating cations during the polymerization process. A noticeable deviation from the Bernoullian statistic could thus be expected.

On the basis of the stereo-sequence assignment reported in the previous section the proportion of the tetrad and pentad peaks of the β -methylene and side-methylene carbon resonances have been determined for polyEVE prepared either in bulk or in benzene and in diethyl ether


Figure 4 62.89 MHz ^{13}C n.m.r. spectra of polyEVE prepared under γ -ray irradiation. (a) Polymerization in the bulk at 20°C ; (b) polymerization in CH_2Cl_2 at 20°C . Spectra in CDCl_3 at 20°C (10 000 transients)

solutions. No significant variation in the relative stereo-sequence intensities was observed for all the samples prepared in low polar media. The expanded ^{13}C n.m.r. spectra of the sample prepared in bulk is given in *Figure 4a*, as representative of the series. The observed and the theoretical stereo-sequence intensities, calculated according to Bernoullian and first order Markovian statistics, are given in *Table 2*. The results clearly show much closer agreement between the experimental data and the first order Markov model, than with the Bernoullian model. The fact that the radiation polymerization of EVE obeys Markovian statistics can be

Table 2 Bernouillian and first order Markov trials for the representation of the configurational sequences in the polyEVE prepared under radiation in bulk

Sequences	Observed	Bernouilli ($P_m = 0.52$)	First order Markov ($P_{r/m} = 0.7$ $P_{m/r} = 0.61$)
Diads			
(m)	0.52		
(r)	0.48		
Triads			
(mm)	0.21	0.27	
(mr)	0.65	0.50	
(rr)	0.14	0.23	
Tetrads			
(mmm)	0.07	0.14	0.08
(mmr)	0.25	0.26	0.25
(rmr)	0.20	0.13	0.20
(mrm)	0.20	0.24	0.23
(mrr)	0.26	0.12	0.20
(rrr)	0.01	0.11	0.04
Pentads			
(mm)	0.21	0.27	0.23
(mmrm)	0.23	0.14	0.20
(mrmr)	0.22	0.13	0.28
(rmrr)	0.11	0.12	0.09
(mmrr)	0.09	0.13	0.07
(rr)	0.22	0.36	0.19

considered as a further argument for a defined stereo-structure of the active chain ends. Since, in the irradiated systems counterions are absent, these results are consistent with a specific interaction between the growing cations and one component of the mixture, most probably with some of the oxygen atoms of the polymer chains.

PolyEVE, prepared by radiation polymerization in methylene dichloride solution, has also been examined by ^{13}C n.m.r. In this solvent, kinetic data lead us to propose that the specific interaction of the cations with the chain was replaced by a predominant solvation by the methylene chloride molecules. Unfortunately, as shown in Figure 4b, the spectrum was poorly resolved, preventing any stereo-sequence measurement. It is probable that the much higher total doses required to get the polymer into this solution also leads to excessive radiation damage including degradation and branching.

Poly(isopropyl vinyl ether)

Assignments of the different resonances to the carbon of polyIPVE have already been achieved by Matsuzaki *et al.*⁹ However, the ^{13}C n.m.r. spectra, obtained at 25 MHz, were not sufficiently resolved to allow any stereo-sequence assignment. We re-examined this polymer at higher fields and the expanded ^{13}C n.m.r. spectra of the α -methine, side-methine and β -methylene carbons of polymers prepared with BF_3OEt_2 and γ -ray initiations are compared in Figure 5. Sharp splits corresponding to stereochemical configuration effects are clearly shown. According to the experimental polymerization conditions, the three peaks of the α -CH may be reasonably assigned to rr, mr and mm triads in order of increasing field strength. The side-methine resonance pattern consists of three main peaks sensitive to longer sequence effects. It has been reported that at lower field strengths⁹, the relative intensities of these main peaks could not be explained by a simple triad effect. This is probably due to overlapping pentad resonances. Based on the preferential

formation, with BF_3OEt_2 initiators, of the isotactic polymer in low polar solvents, some of the isotactic rich sequences can be found at the centre of the O-CH pattern. It is interesting to note that isotactic sequences of the O-CH₂ pattern resonance of polyEVE are observed at higher field strengths while a completely reverse situation has already been reported for poly(terbutyl vinyl ether)⁹. This situation probably justifies the important overlapping of stereo-sequences observed in the polyIPVE isopropoxy resonance. The β -methylene pattern also splits into a complex resonance, corresponding to unresolved stereo-sequences longer than diads. The racemic rich sequences are seen to shift at lower fields than the meso rich sequences but further assignments could not be made.

In conclusion the ^{13}C n.m.r. microstructural determination of polyEVE and polyIPVE prepared under different experimental conditions has been performed at high field strengths. Long stereo-sequence assignments were conducted for polyEVE allowing determination of the configurational statistics of propagation in the polymerization of EVE induced by irradiation in low polar solvents. Good agreement with Markovian model statistics was observed, indicating the occurrence of a penultimate effect. These results are consistent with the postulated existence of a specific interaction between the

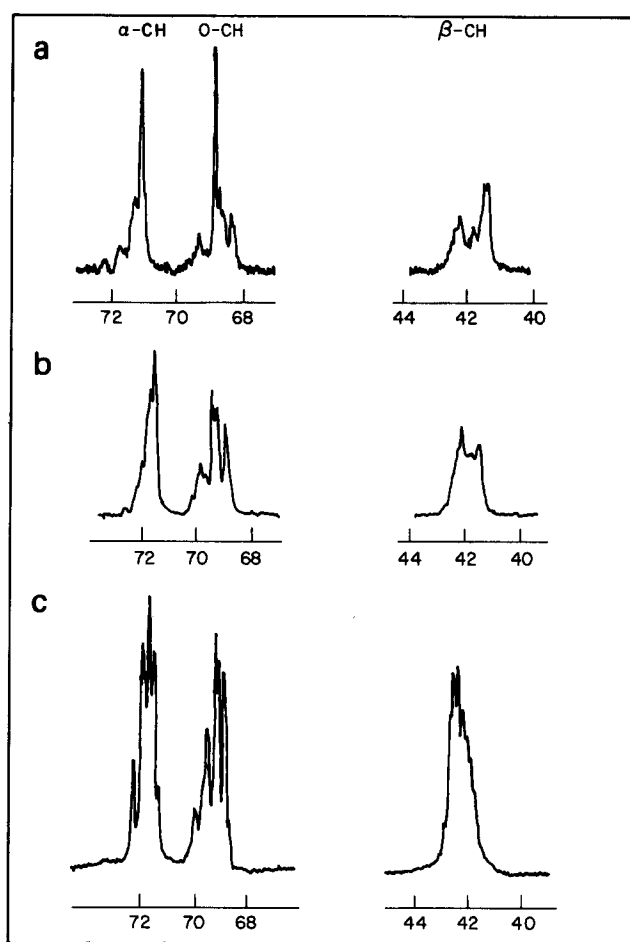


Figure 5 62.89 MHz ^{13}C n.m.r. spectra of polyIPVE. (a) PolyIPVE 1 prepared with BF_3OEt_2 in toluene at -78°C . (b) PolyIPVE 2 prepared with BF_3OEt_2 in CH_2Cl_2 at -78°C . (c) PolyIPVE 3 prepared by irradiation in bulk at 0°C . Spectra in CDCl_3 at 20°C (10 000 transients)

growing cations and, more probably, some oxygen atom of the polymer chain. Due to the complex overlapping of stereo-sequences in polyIPVE, a similar study could not be successfully developed.

ACKNOWLEDGEMENT

The authors would like to acknowledge Professor G. Sauvet for the curve resolution program.

REFERENCES

- 1 Williams, F., Hayashi, Ka., Ueno, K., Hayashi, K. and Okamura, S. *Trans. Faraday Soc.* 1967, **63**, 1501
- 2 Williams, F. 'Fundamental Processes in Radiation Chemistry' (Ed P. Ausloos) Interscience Publishers, New York, 1968
- 3 Deffieux, A., Hsieh, W. C., Squire, D. R. and Stannett, V. *Polymer* 1981, **22**, 1575
- 4 Deffieux, A., Hsieh, W. C., Squire, D. R. and Stannett, V. *Polymer* 1982, **23**, 65
- 5 Hsieh, W. C., Deffieux, A., Squire, D. R. and Stannett, V. *Polymer* 1982, **23**, 427
- 6 Deffieux, A., Young, J. A., Hsieh, W. C., Squire, D. R. and Stannett, V. *Polymer* 1983, **24**, 573
- 7 Deffieux, A., Stannett, V., Wang, A., Young, J. A. and Squire, D. R. *Polymer* 1983, **24**, 1469
- 8 Subira, F., Sauvet, G., Vairon, J. P. and Sigwalt, P. *J. Polym. Sci., Polym. Symp. Edn.* 1976, **56**, 221
- 9 Matsuzaki, K., Ito, H., Kawamura, T. and Uryu, T. *J. Polym. Sci., A-1* 1973, **11**, 971
- 10 Cram, D. J. and Kopecky, K. R. *J. Am. Chem. Soc.* 1959, **81**, 2748
- 11 Pino, P. and Suter, U. W. *Polymer* 1976, **17**, 977
- 12 Bovey, F. A. 'High Resolution NMR of Macromolecules', Academic Press, New York (1972) p. 151
- 13 Matsuzaki, K., Ichijo, C. and Kanai, T. *Makromol. Chem.* 1981, **182**, 2919