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INTRODUCTION



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¹³C-NMR ANALYSIS OF POLYVINYL CHLORIDE SYNTHESIZED WITH MANGANESE(III)DIACETYLACETONATE RHODANIDE AS INITIATOR

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Configurational analysis was made of polyvinyl chloride (PVC) synthesized with manganese(III)diacetylacetonate rhodanide initiated polymerization. The Bernoullian probabilities for meso addition on monomer units were found to be 0.434 from methine, and 0.450 calculated from methylene ¹³C atoms. The results suggest radical polymerization mechanism.

Key words: polyvinyl chloride; organometallic initiators; configurational analysis; manganese(III)diacetylacetonate rhodanide

INTRODUCTION

Polymerization processes carried out with organometallic initiators (OI) were found to give polymers with a more regular structure than the polymers obtained by using other free radical initiators. It is believed that this is due to the coordination mechanism of the polymerization process. In our previous work the results from ¹³C-NMR structure analysis of polyacrylonitrile synthesized by manganese(III)diacetylacetonate rhodanide as initiator were given [1, 2], indicating atactic structure, but with a slightly higher concentration of syndiotactic

sequences as compared to the polymers synthesized by ordinary free radical initiators.

No data were found in the literature concerning the manganese(III)diacetylacetonate rhodanide initiated polymerization of vinyl chloride (VC).

In this work an analysis of the molecular structure of PVC synthesized by using manganese(III)diacetylacetonate rhodanide is given.

The results are compared to those obtained by persulphate (PS) synthesized PVC.

EXPERIMENTAL PART

The ¹³C-NMR spectra are recorded on Fourier transform VARIAN VXR-300 pulsed spectrophotometers, operating at 75.6 MHz for ¹³C resonances. The measurement conditions were: spectral width 16 501 Hz, acquisition time 2 s, 90° pulse and number of pulses 15 000. The samples were desolved in DMSO-d₆ and the operating temperature was 90 °C. Calculations were made from areas for the same functional groups in the NMR spectra. The differences at T₁ for carbons from the same group but in different configurational sequences are insignificant [3].

The peaks in spectra are approximated with Lorentz's functions, with a Lab Calc PC program.

Polymers were obtained by polymerization in suspension.

The polymerization was initiated by manganese(III)diacetylacetonate rhodanide and carried out in laboratory conditions. The initiator (0.003 mol) was added to the monomer (1 mol). The pH was 3.2. The reaction was carried out at the temperature of 313 K for 5 hours, with mixing of 600 rpm. The polymer obtained had a K value of 85.

Suspension PVC, a commercial product of OHIS (SO 721), K value of 70, was used for comparative purposes.

RESULTS AND DISCUSSION

The number of peaks in ^{13}C spectra of vinyl polymers depends on the configuration. Methine spectra show triad configurational sensitivity. There are three groups of peaks (Fig. 1) from syndio, racemic and heterotactic configurational sequences [4]. The areas of peaks (mm, mr and rr), are proportional to the molar ratios of their sequences.

By equation (1) we calculated values of Bernoullian probabilities for the meso addition of monomer units for triad sequences [4].

$$P_m = mn + mr/2 \quad (1)$$

$$4(mm)(rr)/(mr)^2 = 1 \quad (2)$$

The results are given in Table 1 and relation 2 was held satisfactorily as listed in the Table.

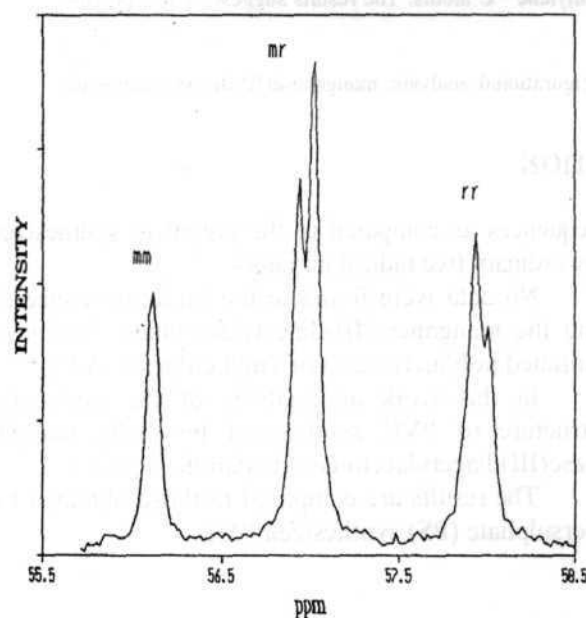


Fig. 1. ^{13}C methine NMR spectrum of PVC synthesized with $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{CNS})$ as initiator

Table 1

The triad microtacticity of PVC

Triads	PVC-PS		PVC- $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{CNS})$		$4(mm)(rr)/(mr)^2$
	exp.	*calc.	exp.	**calc.	
mm	0.195	0.201	0.197	0.188	1.1
mr	0.493	0.480	0.474	0.491	
rr	0.318	0.312	0.335	0.320	

* $P_m = 0.443$, ** $P_m = 0.434$

The methylene ^{13}C -spectrum shows tetrad configurational sensitivity. Six peaks exist in this part of spectrum (Fig. 2). The assignment of these peaks was made on the basis of Inane work [5, 6] and the calculated molar areas from Bernoullian statistics [7, 8]. The agreement between the calculated and the experimental values is fairly good (Tab. 2).

Bernoullian probabilities for meso addition were calculated by the equations for the relation between triad, and tetrad sequences (equations 3 and 4) and then by the equation 1.

$$mm = mmm + mmm/2 \quad (3)$$

$$mr = rmr + mrm + (mmr + mrr)/2 \quad (4)$$

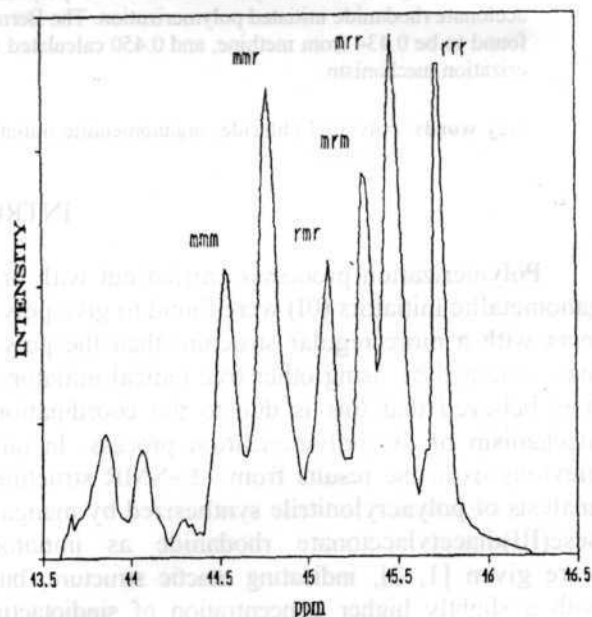


Fig. 2. ^{13}C methylene NMR spectrum of PVC synthesized with $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{CNS})$ as initiator

Table 2

The tetrad microtacticity of PVC

Tetrad	PVC-PS		PVC- $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{CNS})$	
	exp.	*calc.	exp.	**calc.
rrr	0.159	0.146	0.177	0.167
mrr	0.242	0.262	0.256	0.272
mrm	0.109	0.118	0.107	0.111
rmr	0.138	0.131	0.134	0.136
mmr	0.246	0.236	0.230	0.222
mmm	0.104	0.106	0.095	0.090

* $P_m = 0.473$, ** $P_m = 0.450$

The values for Bernoullian probabilities for meso addition found from both types of ¹³C atoms show good agreement. The values of concentration of syndiotactic sequences are higher than the isotactic ones for a polymer produced with both initiators. The concentration of syndiotactic sequences for polymer synthesized with manganese(III)diacetylacetonate rhodanide is slightly higher than that of the polymer produced with persulphate.

The conclusions coincide with our previous work concerning the possibility of more than one polymerization mechanisms existing, but the major

one is free radicals [1, 2]. The small peaks in the methine spectra are designed as structural impurities. The most probable structure is branching [5, 9]. The methylene groups adjacent to the branch are different from other methylene groups in the polymer.

Each branch point will influence the resonances of at least three methylene carbons. The number of branch points per 100 monomer units were 4 and 5 for PVC produced by persulphate and PVC produced by Mn(C₅H₇O₂)₂(CNS) respectively.

CONCLUSION

From the ¹³C-NMR spectra which show triad and tetrad sensitivity, we made configurational analysis of PVC, synthesized with Mn(C₅H₇O₂)₂(CNS) as initiator. The Bernoullian probabilities for meso

addition of the monomer units are calculated as 0.434 from methine and 0.450 from methylene ¹³C atoms. The results show that the mechanism of polymerization is mainly a free radical in nature.

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Резиме

¹³C-NMR АНАЛИЗА НА ПОЛИВИНИЛХЛОРИД СИНТЕТИЗИРАН СО МАНГАН(III)АЦЕТИЛАЦЕТОНАТ РОДАНИД

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Клучни зборови: поливинилхлорид; органометални иницијатори; конфигурациска анализа; манган(III)диацетилацетонат роданид

Одредени се Bernoullian-овите веројатности за мезо-аддиција на мономерната единица на PVC добиен со манган(III)ацетилацетонат роданид како иницијатор. Тие се слични со вредностите за PVC добиен со радика-

лен механизам. Тоа укажува дека механизмот на полимеризација со манган(III)ацетилацетонат роданид како иницијатор е, главно, радикален.

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