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¹³C NMR ANALYSIS OF POLYACRYLONITRILE SYNTHESIZED WITH MANGANESE(III) DIACETYLACETONATE RHODANIDE AS INITIATORS

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Configurational analyses of polyacrylonitrile polymerized with manganese(III) diacetylacetonate rhodanide at higher temperature have been made. The Bernoullian probability for meso addition on the monomer units in the polymer chain is 0.5237 from methine and 0.539, from nitrile ¹³C atoms, and the corresponding average number lengths of the meso sequences (\bar{n}_p) are 2.196 and 2.1. The results are similar to those for polymers produced in a free radical process. They show that polymers are atactic and that the mechanism of polymerisation, under these conditions, is radical.

Key words: polyacrylonitrile, organometallic initiators, configurational analysis, manganese(III) diacetylacetonate rhodanide

INTRODUCTION

Certain organometallic initiators usually produce polymers with more a regular structure than do the free radical initiators, due to the coordination mechanism of polymerization.

The mechanism of polymerization with manganese(III) diacetylacetonate rhodanide is not known, since this is the first time it has been as an initiator and there are no data about the molecular structure of polymers produced by this initiator.

The best method of determining polymer molecular structure is by analysis of their NMR spectra. Compared to proton, ¹³C spectra are more sensitive on the configuration, they are simpler and the polymer configuration can be expressed in terms of triads, tetrads, pentads etc. [1, 2].

In this study configurational analyses of polyacrylonitrile produced with manganese(III) diacetylacetonate rhodanide and azoisobutyronitrile (AIDN) as initiators are given.

EXPERIMENTAL

The ¹³C spectra were recorded on the Fourier transform VARIAN VXR-300 pulsed spectrophotometers, operating at 75.6 MHz for ¹³C resonances. The measurement conditions were: spectral width 16501 Hz, acquisition time 2 s, 90° pulse and number of pulses 12,000. The samples were dissolved in DMSO-d₆ and the operating temperature was 90 °C.

Calculations were made from areas in the same functional groups in NMR spectra. In carbons from the same group but in different configurational sequences the differences at T_1 are insignificant [3].

Traces in spectra were approximated with Lorentz's functions. Reliability factors are calculated by the equation:

$$R = \left(\frac{\sum (f_{\text{exp}} - f_{\text{calc}})^2}{\sum f_{\text{exp}}^2} \right)^{1/2} \quad (1)$$

where f_{exp} are experimental and f_{calc} calculated values. All calculations were made on the PC computer.

Polymerizations were carried out at 60 °C using Mn(C₅H₇O₂)₂(NCS) and AIDN as inhibitors.

RESULTS AND DISCUSSION

The number of peaks characterizing any group of the vinyl polymers on the NMR spectra depends on the configurational sensitivity.

In the range where there are peaks from methine carbons, three peaks from different configurational sequences exist in ¹³C polyacrylonitrile spectra

(Fig.1). This number of peaks is characteristic of the triad configurational sensitivity of methine groups.

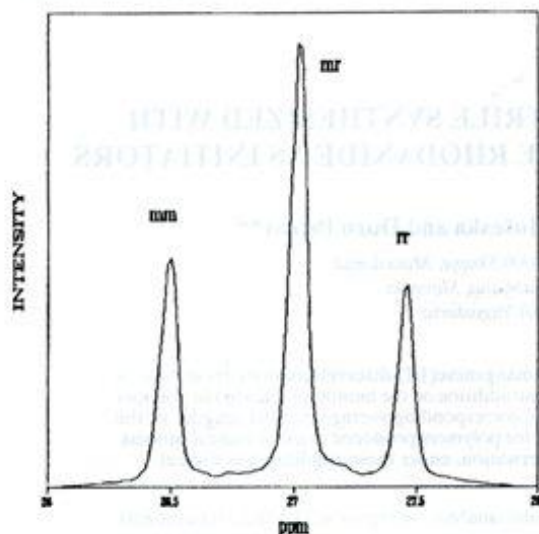


Fig. 1. ^{13}C methine NMR spectrum of polyacrylonitrile synthesized with $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{NCS})$

For segments of $-\text{CH}_2-\text{CHR}-$ type vinyl polymers (where R is of medium size) vinyl polymers with the same configuration, the conformation in solution is qualitatively the same [4]. The consequence of this is the same order of peaks belonging to different configurational sequences [5].

The order of peaks which belong to the triad sequences, from methine ^{13}C atoms are syndio (rr), hetero (mr) and isotactic (mm), from higher to lower values on the chemical shift [5-7].

We have reproduced the spectra by Lorentz's functions and have found molar areas, which are proportional to the molar ratios of configurational sequences.

Table 1 shows the results from analysis of peaks using methine ^{13}C as polymer, produced by two types of initiators.

Table 1
Configurational analysis for polyacrylonitrile produced by different initiators, made on the basis of methine ^{13}C .

Triads	AIDN		$\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{CNS})$	
	exp.	calc.	exp.	calc.
	$P_m = 0.5320$		$P_m = 0.5237$	
mm	0.2800	0.2830	0.2659	0.2742
mr	0.5040	0.4979	0.5101	0.4988
rr	0.2010	0.2190	0.2238	0.2330
	$\bar{n}_m = 2.1360$		$\bar{n}_m = 2.1000$	

From molar areas (mm and mr) we calculated the Bernoullian probability for meso addition (P_m) and the average sequence length number (\bar{n}_m) by equations:

$$P_m = (\text{mm}) + 1/2(\text{mr}) \quad (2)$$

$$\bar{n}_m = 1/(1 - P_m) \quad (3)$$

In the high resolution spectra of PAN, in the part of the spectar from cyanide ^{13}C atoms, three groups of peaks exist (Fig.2). The number of traces in the group depends on the number of pentads in them [8]. The order of triads in the spectra is opposite to that found in the methine one, and is mm, mr and rr from higher to lower values of chemical shifts [6].

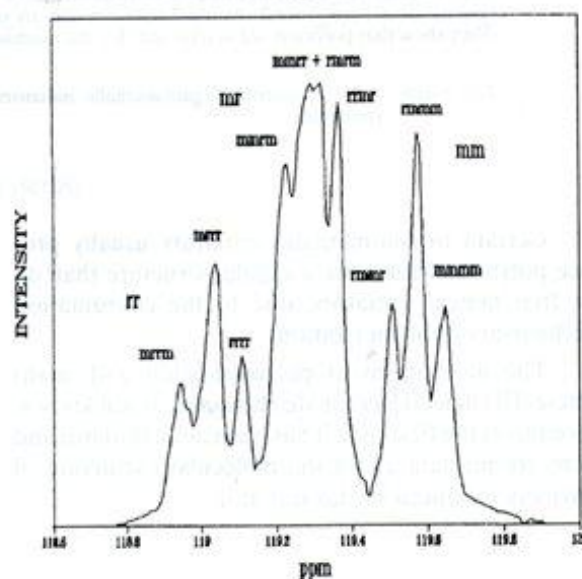


Fig. 2. ^{13}C nitrile NMR spectrum of polyacrylonitrile synthesized with $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{NCS})$

The resolution between the nearest peaks from different triads is 0.148 (between mm and mr) and 0.144 ppm (between mr and rr). The differences between peaks in triads are from 0.022 to 0.096 ppm. The results of configurational analysis using nitrile ^{13}C in terms of triad and pentad sequences are shown in table 2.

The intensities conform to Bernoullian's statistics, and from both tables a good agreement, between the found and calculated values for carbons in the two different functional groups can be seen.

It is known that PAN synthesized with organo-metallic initiators is a partly lower soluble polymer, which is a consequence of its crystal (stereoregular) structure. At a higher temperature it has better solubility and the polymer stereoregularity in the

Table 2

Configurational analysis of polyacrylonitrile synthesized with $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{NCS})$ made on the basis of nitrile ^{13}C

Triads	Exper.	Calc.	Pentads	Exper.	Calc.
mm	0.2777	0.2900	mmmm	0.0813	0.0814
			rmmm	0.1360	0.1445
			rmmr	0.0604	0.0617
mr	0.5228	0.4970	rrmr	0.1127	0.1055
			mmrr		0.1234
			+	0.2486	
			rmmm		0.1234
			mrrm	0.1614	0.1444
m	0.2000	0.2123	rrrr	0.0406	0.0451
			mrrr	0.1023	0.1131
			mrrm	0.0564	0.0722

$P_m = 0.5392$ $\bar{n}_m = 2.1960$

solution (9) rises. The polymers studied are completely soluble in DMSO-d_6 and the results from ^{13}C spectra give reliable insight in the structure of the polymers.

The structures of the polymers which are polymerized by free radical initiators and $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{NCS})$ are similar. The concentration of the heterotactic (mr) sequences is highest and the concentration of isotactic (mm) is somewhat higher than the syndiotactic sequences.

The polymer produced with $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{NCS})$ as initiator has slightly higher syndiotactic sequences concentration.

Accordingly the conclusion can be drawn that under these conditions of polymerization the polymerization mechanism is free radical by nature.

CONCLUSIONS

On the basis of ^{13}C spectra, which show triad and pentad sensitivity, we have made a configurational analysis of polyacrylonitrile synthesized with manganese(III) diacetylacetonate rhodanide as initiator. The Bernoullian probabilities are found for meso addition of monomer units are calculated as 0.539

using methine and 0.5237 using nitrile ^{13}C atoms. These values are similar to the results for polymers produced by free radical initiators (AIDN). The results show that the mechanism of polymerization under these conditions is mainly free radical by nature.

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Резиме

^{13}C -NMR АНАЛИЗА НА ПОЛИАКРИЛОНИТРИЛ СИНТЕТИЗИРАН СО $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{NCS})$ КАКО ИНИЦИЈАТОР

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Клучни зборови: полиакрилонитрил; органометален иницијатор; конфигурациона анализа; манган(III)диацетилацетонат роданид

Направена е конфигурациона анализа на полиакрилонитрил полимеризиран со $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{NCS})$ како иницијатор на повисока температура. Пресметани се Bernoullian-овата веројатност за мезоадисија на мономерната единица и

средната должина на мезосегментите. Тие се слични со вредностите за полимери добиени по радикален механизам. Тоа укажува дека механизмот на полимеризација со $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{NCS})$ како иницијатор главно е радикален.

ГЛАСНИК НА ХЕМИЧАРИТЕ И ТЕХНОЛОЗИТЕ НА МАКЕДОНИЈА

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