

M. PASICH¹, M. SIOŁEK^{2,3}, N. HENZEL⁴, M. MATLENGIEWICZ²

¹Institute for Engineering of Polymer Materials and Dyes, Paint and Plastics Department, ul. Chorzowska 50A, 44-100 Gliwice, Poland
e-mail: m.pasich@impib.pl

²University of Silesia, Institute of Chemistry, ul. Szkolna 9, 40-006 Katowice, Poland

³Synthos S.A., ul. Chemików 1, 32-600 Oświęcim, Poland

⁴Silesian Technical University, Institute of Electronics, ul. Akademicka 16, 44-100 Gliwice, Poland

Microstructural analysis of poly(*n*-propyl acrylate) and poly(isopropyl acrylate) based on the backbone β -methylene carbon signal in the ^{13}C NMR spectra

Abstract: The samples of poly(*n*-propyl acrylate), PnPrA, and poly(isopropyl acrylate), PiPrA, were synthesized by free radical polymerization in solution (butan-2-one). The 100 MHz ^{13}C NMR spectra of these homopolymers were recorded in two deuterated solvents: chloroform (CDCl_3) and benzene (C_6D_6). In the PnPrA spectra, the backbone β -methylene carbon signal ($\beta\text{-CH}_2$) (33.0 – 36.5 ppm) was split up to configurational hexads for CDCl_3 and C_6D_6 . In the PiPrA spectra, the $\beta\text{-CH}_2$ signal (32.5 – 36.5 ppm) was split up to configurational hexads in both solvents.

Keywords: poly(*n*-propyl acrylate), poly(isopropyl acrylate), microstructure, NMR spectroscopy

ANALIZA MIKROSTRUKTURALNA POLI(AKRYLANU N-PROPYLU) I POLI(AKRYLANU IZOPROPYLU) NA PODSTAWIE SYGNAŁU WĘGLA B-METYLENOWEGO W WIDMACH ^{13}C NMR

Streszczenie: Próbki poli(akrylanu *n*-propylu), PnPrA, i poli(akrylanu izopropylu), PiPrA, otrzymano w polimeryzacji rodnikowej w roztworze. Widma 100 MHz ^{13}C NMR tych homopolimerów zarejestrowano w dwóch deuterowanych rozpuszczalnikach: chloroformie (CDCl_3) i benzenu (C_6D_6). Na widmach PnPrA, zarejestrowanych w deuterowanym chloroformie i benzenu sygnał węgla metylenowych ($\beta\text{-CH}_2$) (33,0 – 36,5 ppm) ulega rozszczepieniu się na poziomie heksad konfiguracyjnych, natomiast sygnał $\beta\text{-CH}_2$ (32,5 – 36,5 ppm) poli(akrylanu izopropylu) rozszczepia się na poziomie heksad konfiguracyjnych.

Słowa kluczowe: poli(akrylan *n*-propylu), poli(akrylan izopropylu), mikrostruktura, spektroskopia NMR

INTRODUCTION

Acrylic polymers found many industrial applications as optical, engineering and biomedical materials as well as paints, glues, and finishing materials in building industry, due to wide range of interesting physicochemical properties. These properties are strongly influenced by microstructure of the polymer chain, i.e., its stereochemistry and distribution of repeating units along the chain. Moreover, the polymer properties can be modified by copolymerization reaction and

acrylate-methacrylate copolymers are widely used in industry and hi-tech applications. Tailoring of a copolymer properties requires precise knowledge on the macromolecular chain structure and the nuclear magnetic resonance spectroscopy (NMR) of liquids is practically the only analytical technique providing deep insight into such details of the chemical structure of the macromolecular chains of synthetic polymers. Analysis of various acrylic copolymer requires the data on the microstructure of individual acrylic homopolymers. Literature survey indicated that homopolymers of propyl acrylates

as well as their copolymers were scarcely studied by ^{13}C NMR [1-3] therefore, the aim of our work was to perform detailed microstructural analysis of both poly(propyl acrylates), necessary to study microstructure of the acrylic copolymers comprising the propyl acrylate units.

For acrylic polymers two signals in the ^{13}C NMR spectra are of predominant interest from microstructural point of view: the carbonyl and the methylene carbon ($\beta\text{-CH}_2$); since they are present in all typical acrylic structures and provide complete information on all sequences - the carbonyl signal on distribution of uneven sequences, while the methylene signal from the main chain on distribution of even sequences [4-13].

Accurate assignment of individual lines to respective sequences is vital in detailed analysis, especially, when longer sequences are taken into account. The correctness of the attribution can be verified by spectral simulation, however, the intensity and exact position of a line representing given sequence has to be known. Relative intensities may be calculated assuming Bernoulli or Markov distribution, while the values of chemical shifts may be determined by incremental calculations, and such an approach has been shown effective in the study of both carbonyl and $\beta\text{-CH}_2$ signals [14-18].

EXPERIMENTAL

The samples of poly(*n*-propyl acrylate), PnPrA, and poly(isopropyl acrylate), PiPrA, were synthesized by radical polymerization in solution [13-18]. The monomer was mixed with butan-2-one to obtain 40% wt. solution and was heated up to 80°C. Then, azobisisobutyronitrile (AIBN) was added as radical initiator (0.5%wt. with respect to the total solution). The polymerization mixture was diluted with acetone and poured into a large volume of a water-methanol mixture to precipitate the polymer, which was then washed with methanol and vacuum dried to constant weight.

The 100 MHz ^{13}C NMR spectra were recorded with a Bruker AM 400 spectrometer at 40°C, using sample concentration of 10% (w/v) in benzene- d_6 and CDCl_3 as the solvents. Good signal to noise ratio was obtained for about 12000 scans, with a 4 s delay.

Simulations of the NMR spectra were performed using our own software written in Matlab environment (MathWorks, Inc.).

RESULTS AND DISCUSSION

The β -methylene carbon signal of poly(*n*-propyl acrylate), PnPrA

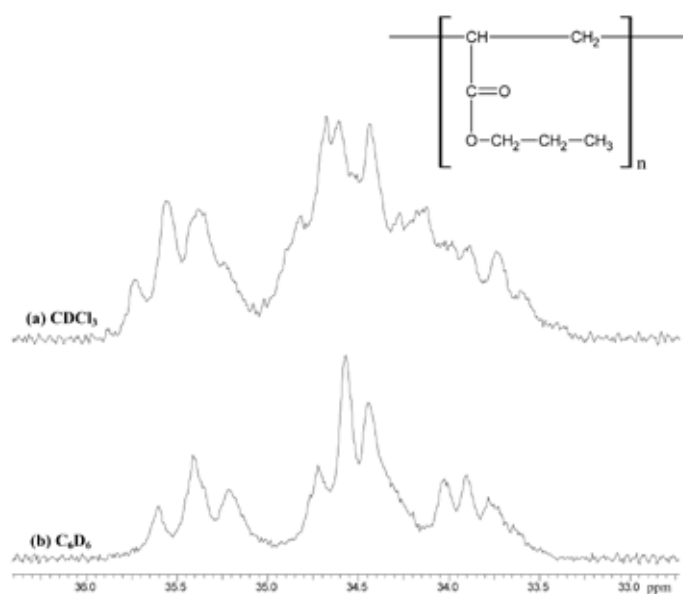


Figure 1. 100 MHz ^{13}C NMR spectrum of the β -methylene carbon signal of PnPrA in CDCl_3 (a) and benzene- d_6 (b)

In the 100 MHz ^{13}C NMR spectra of P*n*PrA (Figure 1) the β -CH₂ signal exhibit lines from 33.0 to 36.5 ppm, with visible traces of splitting due to configurational effects. Application of higher magnetic field can split this signal to display more details on longer sequences.

The triad distribution can be calculated from -OCH₂- signal for P*n*PrA by simple integration, assuming the assignment of triad signals according to Aerdts [13]. We obtained the values of $P(rr)=0.6091$, $P(\overline{mr})=0.3495$ and $P(mm)=0.0414$ indicating predominantly syndiotactic P*n*PrA sample. Probabilities of longer sequences according to Bernoulli and 1st order Markov

statistics can be then readily calculated and used to verify the propagation statistics by simulation of the β -methylene carbon signal. For the sake of consistency with other results we will henceforth use the 1st Markov distribution of configuration sequences as it is usually assumed for acrylic chains.

The correctness of sequence attribution can be verified by spectral simulation. The calculated sequence probabilities can be used as line intensities. They can be estimated applying an incremental procedure described previously [14-18]. Table 1 shows the data necessary for simulation of β -CH₂ signal P*n*PrA in two solvents.

Table 1. Probabilities of hexad sequences of syndiotactic P*n*PrA calculated according to 1st order Markov statistics and chemical shifts calculated incrementally

Probability	1 st order Markov	Chemical shift, δ [ppm]	
		CDCl ₃	C ₆ D ₆
P(<i>mmmmmm</i>)	0.0003	35.78	35.75
P(<i>mmmmmr</i>)	0.002	35.70	35.69
P(<i>rmmmmr</i>)	0.005	35.62	35.63
P(<i>mmmmrm</i>)	0.003	35.40	35.53
P(<i>rmmmrm</i>)	0.012	35.32	35.47
P(<i>mmmmrr</i>)	0.010	35.49	35.47
P(<i>rmmmrr</i>)	0.042	35.41	35.41
P(<i>mrrmr</i>)	0.007	35.01	35.31
P(<i>mrrmrr</i>)	0.049	35.10	35.25
P(<i>rrmrr</i>)	0.085	35.19	35.19
P(<i>mrrmm</i>)	0.001	33.01	33.45
P(<i>mrrmr</i>)	0.012	33.11	33.51
P(<i>rrmr</i>)	0.025	33.21	33.57
P(<i>mrrmm</i>)	0.012	33.88	34.16
P(<i>mrrmr</i>)	0.049	33.98	34.22
P(<i>rrrmm</i>)	0.040	33.72	34.01
P(<i>rrrmr</i>)	0.171	33.82	34.07
P(<i>mrrrm</i>)	0.024	34.75	34.87
P(<i>mrrrr</i>)	0.164	34.59	34.72
P(<i>rrrrr</i>)	0.286	34.43	34.57

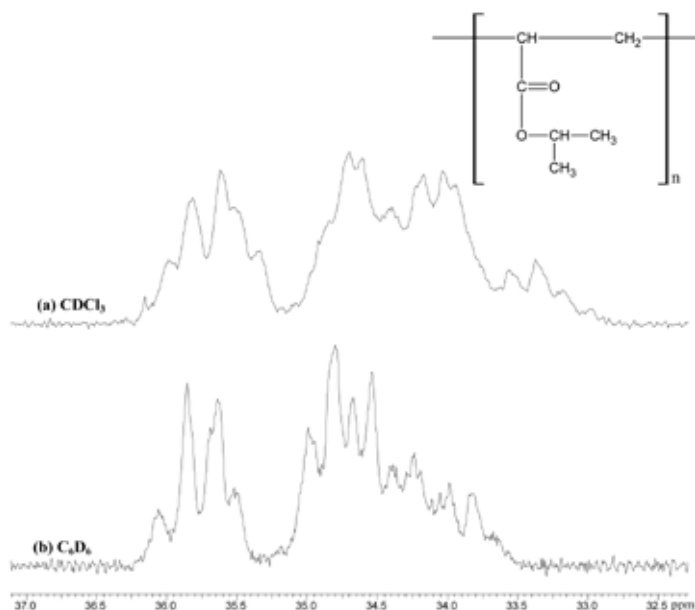


Figure 4. 100 MHz ^{13}C NMR spectrum of the β -methylene carbon signal of PiPrA in CDCl_3 (a) and benzene- d_6 (b)

Table 2. Probabilities of configurational hexads for syndiotactic PiPrA calculated according to 1st order Markov statistics and chemical shifts calculated incrementally

Probability	1 st order Markov	Chemical shift, δ [ppm]	
		CDCl_3	C_6D_6
$P(\overline{mmmmmm})$	0.0004	36.16	36.23
$P(\overline{mmmmmr})$	0.003	36.08	36.15
$P(\overline{rmmmr})$	0.006	36.00	36.07
$P(\overline{mmmrmm})$	0.004	35.75	35.80
$P(\overline{rmmrm})$	0.014	35.67	35.72
$P(\overline{mmmr\bar{r}})$	0.011	35.87	35.94
$P(\overline{rmmr\bar{r}})$	0.045	35.79	35.86
$P(\overline{mrmmr})$	0.008	35.33	35.36
$P(\overline{mrmmr\bar{r}})$	0.054	35.45	35.50
$P(\overline{rrmmr})$	0.085	35.57	35.64
$P(\overline{mmrmm})$	0.002	32.99	33.55
$P(\overline{mmrmm\bar{r}})$	0.014	33.18	33.67
$P(\overline{rmmr\bar{r}})$	0.028	33.37	33.79
$P(\overline{mrrmm})$	0.013	34.02	34.37
$P(\overline{mrrm\bar{r}})$	0.054	34.21	34.49
$P(\overline{rrrmm})$	0.043	33.83	34.18
$P(\overline{rrrmm\bar{r}})$	0.171	34.02	34.30
$P(\overline{mrrrm})$	0.025	35.04	35.18
$P(\overline{mrrr\bar{r}})$	0.162	34.85	34.99
$P(\overline{rrrrr})$	0.258	34.66	34.80

The incremental method of calculating chemical shifts allowed determined of location of even sequences, i.e. dyads, tetrads and hexads. Table 2 shows the data necessary to simulate the $\beta\text{-CH}_2$ signal of PiPrA.

Simulation of the β -methylene signal of poly(isopropyl acrylate) based on the above increment values gives the spectra presented in Figures 5 and 6.

CONCLUSIONS

The 100 MHz ^{13}C NMR spectra of two poly(propyl acrylates), i.e., poly(*n*-propyl acrylate), P*n*PrA, and poly(isopropyl acrylate), PiPrA, recorded in CDCl_3 and C_6D_6 offer good resolution of their β -methylene carbons to observe signals of configurational hexads. Based on the analysis of $\beta\text{-CH}_2$ signal, confirmed by positive

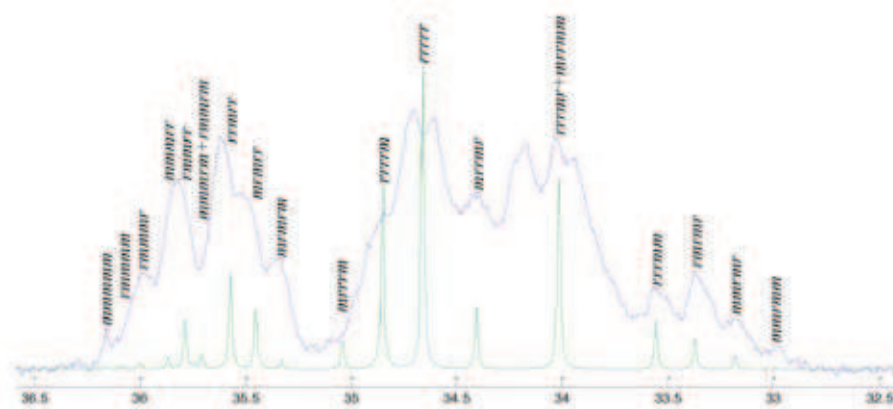


Figure 5. Simulation of the $\beta\text{-CH}_2$ signal of PiPrA in CDCl_3 using 1st order Markov statistics and incremental calculation of chemical shifts at hexad level, linewidth 1 Hz

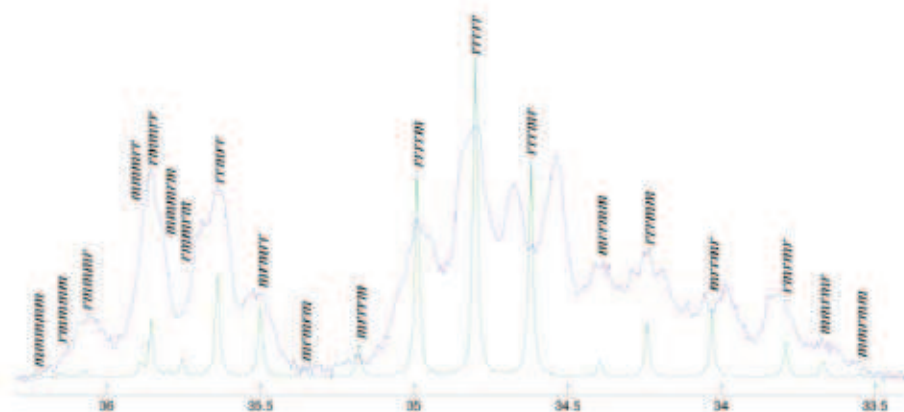


Figure 6. Simulation of the $\beta\text{-CH}_2$ signal of PiPrA in C_6D_6 using 1st order Markov statistics and incremental calculation of chemical shifts at hexad level, linewidth 1 Hz

Simulation of the methylene signal P*n*PrA and PiPrA with these parameters leads to good match of the line positions. In this region of experimental spectrum we also observe four bands, as in the simulated one, but with visibly shifted positions.

spectra simulation, the sequence distribution up to configurational hexads can be determined. It was shown that incremental calculation can be utilized to determine positions of individual hexads. Using two sets of increments, separate for each solvent, it was possible to calculate the chemical shifts of all configurational hexads.

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