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Microstructural analysis of two poly(propyl acrylates): poly(*n*-propyl acrylate) and poly(isopropyl acrylate), based on the carbonyl signal in the ¹³C NMR spectra

Summary: 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 ¹³C NMR spectra of these homopolymers were recorded in two deuterated solvents: chloroform (CDCl₃) and benzene (C₆D₆). In the spectra of both PnPrA and PiPrA recorded in CDCl₃ the carbonyl signal was split at the level of configurational triads, while in C₆D₆ this signal revealed heptad splitting for PiPrA and pentad splitting for PnPrA.

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

ANALIZA MIKROSTRUKTURALNA DWÓCH POLI(AKRYLANÓW PROPYLU): POLI(AKRYLANU *N*-PROPYLU) I POLI(AKRYLANU IZOPROPYLU), NA PODSTAWIE SYGNAŁU WĘGLA KARBONYLOWEGO W WIDMACH ¹³C NMR

Streszczenie: Próbkę poli(akrylanu *n*-propylu), PnPrA, i poli(akrylanu izopropylu), PiPrA, otrzymano w polimeryzacji rodnikowej w roztworze butan-2-onu. Widma 100 MHz ¹³C NMR tych homopolimerów zarejestrowano w dwóch deuterowanych rozpuszczalnikach: chloroformie (CDCl₃) i benzenie (C₆D₆). Na widmach PnPrA i PiPrA, zarejestrowanych w deuterowanym chloroformie, sygnał węgla karbonylowych (C=O) ulega rozszczepieniu na poziomie triad konfiguracyjnych, podczas gdy dla deuterowanego benzenu sygnał C=O PiPrA rozszczepia się na poziomie heptad, a dla PnPrA pentad konfiguracyjnych.

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

INTRODUCTION

Nuclear magnetic resonance spectroscopy of liquids is the only analytical technique providing deep insight into details of the chemical structure of the macromolecular chains of synthetic polymers. [1-10]. For acrylic polymers two signals in the ¹³C NMR spectra are of predominant interest from microstructural point of view: the carbonyl and methylene carbon (β -CH₂); since they are present in all typical acrylic structures and provide complete information on all sequences.

Carbonyl signal is usually observed as a single line for homopolymers of methyl, ethyl or propyl acrylate and there is no splittings due to configurational differences in their ¹³C NMR spectra recorded in CDCl₃ up to 100 MHz [3]. Starting from butyl acrylates configurational effect can be observed with clear splitting up to pentads for poly(*n*-butyl acrylate), PnBuA, and poly(*tert*-butyl acrylate), PtBuA. We have observed that simple change of solvent used in the NMR study, namely, from deuterated chloroform to deuterated benzene, can provide spectra with pronounced

configurational splitting of the carbonyl signal even for the simplest acrylate of the family, i.e., poly(methyl acrylate) [11]. The carbonyl signals of P*n*PrA and PiPrA recorded in benzene exhibit a complex pattern of superimposed configurational sequences at the pentad and heptad level, respectively.

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 [2-4, 7, 11-17].

Acrylic and methacrylic homopolymers and their copolymers constitute an important group used as engineering materials, protective glasses, optical elements, paints, varnishes, plasters and adhesives [18]. Because the physicochemical, mechanical or biological properties of polymers strongly depend on their microstructure, i.e. stereochemistry and regioregularity of the chain, as well as composition and distribution of comonomers along the copolymer the control of the macroscopic properties of the synthesized polymer systems requires good knowledge of the microstructure, hence, such studies have been conducted for a number of the most commonly used polymers, also for acrylic systems [3, 19]. The purpose of this work was therefore to perform microstructural characteristics of next two acrylic homopolymers: poly(*n*-propyl acrylate) and poly(isopropyl acrylate).

EXPERIMENTAL

The samples of poly(*n*-propyl acrylate), P*n*PrA, and poly(isopropyl acrylate), PiPrA, were synthesized by radical polymerization in solution [2-4, 11-15]. 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 carbonyl signal of poly(isopropyl acrylate), PiPrA

Figure 1 shows the 100 MHz ^{13}C NMR spectrum of poly(isopropyl acrylate) recorded in benzene- d_6 , as well as attribution of the polymer carbon signals.

Details of the carbonyl regions of PiPrA homopolymer recorded in different solvents are shown in Fig. 2a (deuterated chloroform) and Fig. 2b (benzene- d_6).

Due to the solvent effects the carbonyl signal of poly(isopropyl acrylate) in C_6D_6 , offers better line separation than that in CDCl_3 , therefore, further analysis will be performed for the spectrum recorded in deuterated benzene.

The triad distribution can be calculated from $-\text{OCH}-$ signal for PiPrA by simple integration [11-13, 15]. We obtained the values of $P(rr)=0.5860$, $P(\overline{m}r)=0.3680$ and $P(mm)=0.0460$ indicating predominantly syndiotactic PiPrA 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

carbonyl 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.

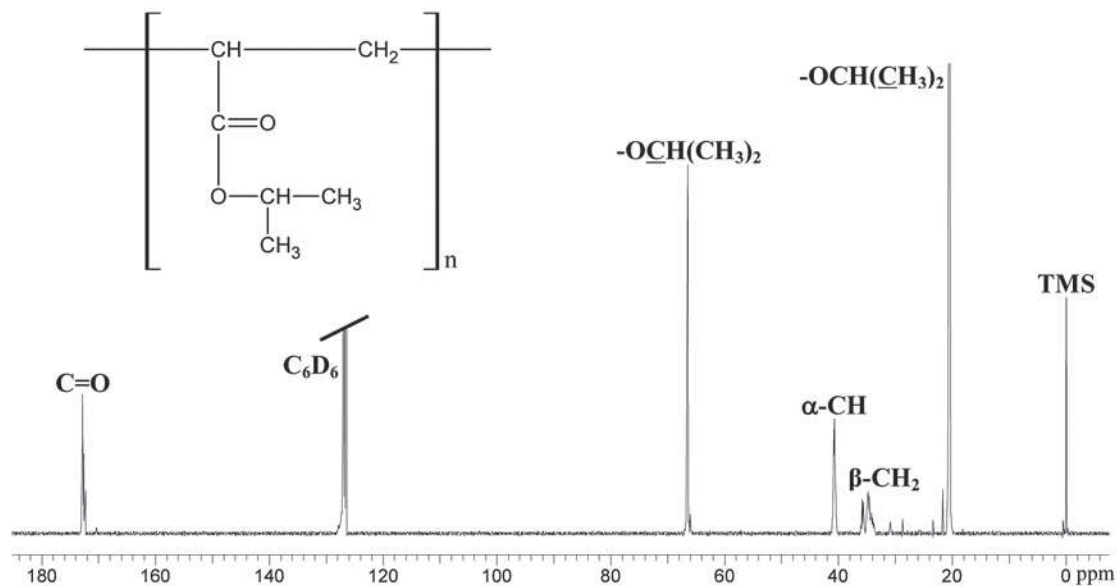


Figure 1. 100 MHz ¹³C NMR spectrum of poly(isopropyl acrylate) recorded in C_6D_6

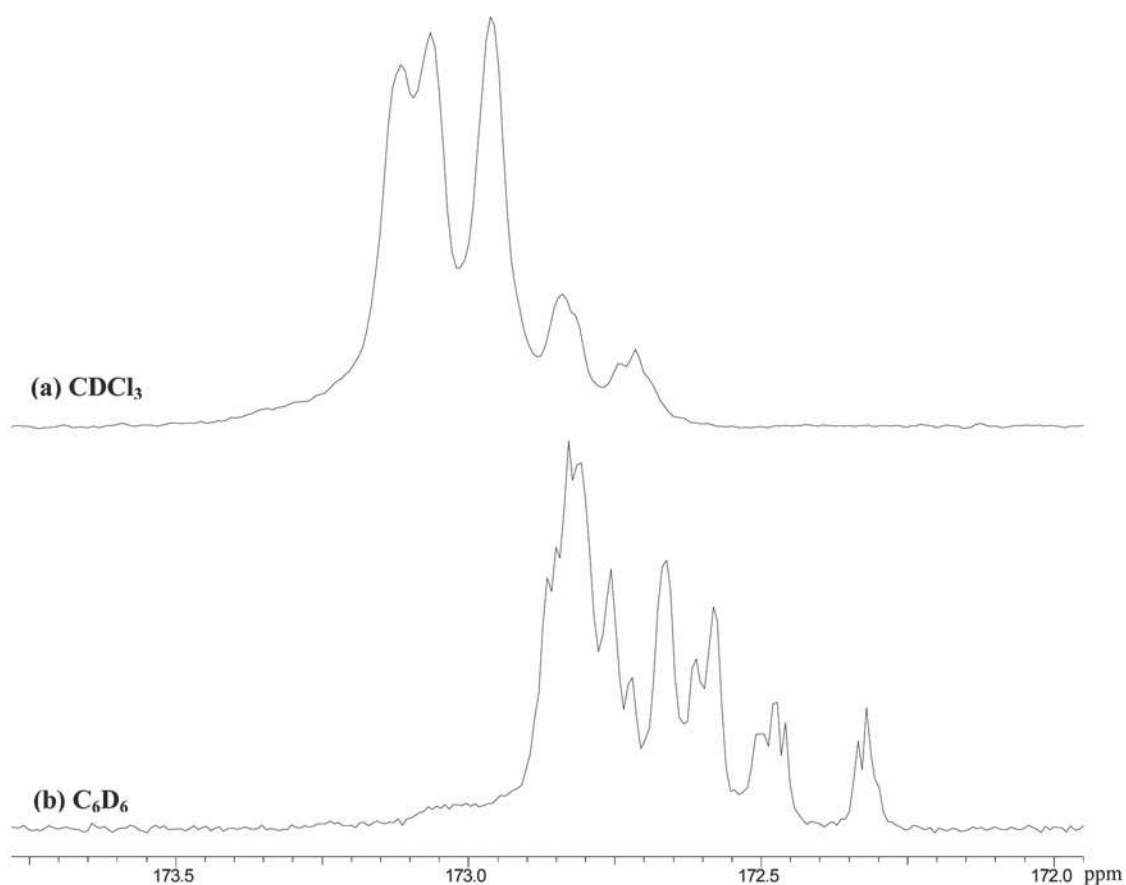


Figure 2. 100 MHz ¹³C NMR carbonyl signal of poly(isopropyl acrylate) recorded in (a) CDCl_3 and (b) C_6D_6

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

Sequence	First-order Markov probabilities	Chemical shift, d [ppm]
P(<i>mmmmmm</i>)	0.0001	172.37
P(<i>rrmmrr</i>)	0.009	172.34
P(<i>mrrmmr</i>)	0.011	172.31
P(<i>rrmmrr</i>)	0.017	172.32
P(<i>rmmrrm</i>)	0.011	172.61
P(<i>mmrrrr</i>)	0.009	172.59
P(<i>rmmrrm</i>)	0.011	172.53
P(<i>rmmrrr</i>)	0.034	172.58
P(<i>mrrmmr</i>)	0.013	172.58
P(<i>rrmrrm</i>)	0.011	172.61
P(<i>rrmrrr</i>)	0.043	172.59
P(<i>mrrrrm</i>)	0.013	172.50
P(<i>mrrrrr</i>)	0.041	172.56
P(<i>rrmrrm</i>)	0.041	172.51
P(<i>rrmrrr</i>)	0.130	172.57
P(<i>mmrrrm</i>)	0.011	172.88
P(<i>rmrrrm</i>)	0.021	172.86
P(<i>mrrrrm</i>)	0.010	172.80
P(<i>rrrrmm</i>)	0.032	172.86
P(<i>mrrrrm</i>)	0.041	172.78
P(<i>rrrrmr</i>)	0.130	172.84
P(<i>mrrrrm</i>)	0.019	172.70
P(<i>mrrrrr</i>)	0.123	172.76
P(<i>rrrrrr</i>)	0.197	172.81

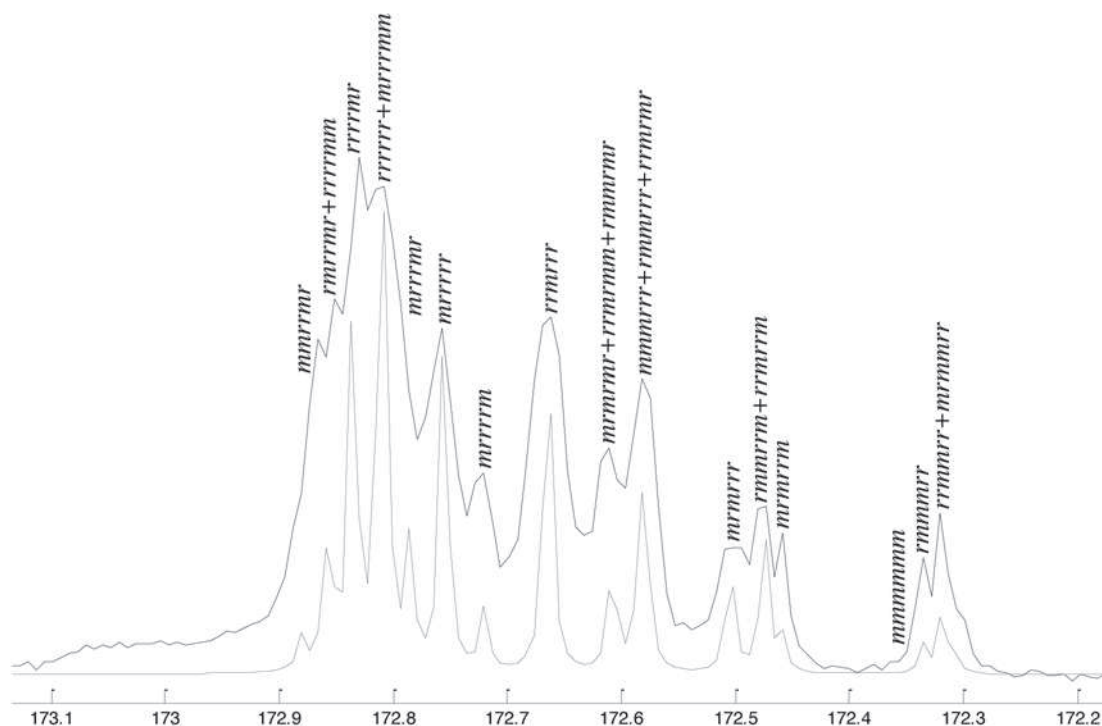


Figure 3. Simulation of the carbonyl signal of PiPrA in benzene- d_6 using 1st order Markov statistics and incremental calculation of chemical shifts at heptad level, linewidth 2 Hz

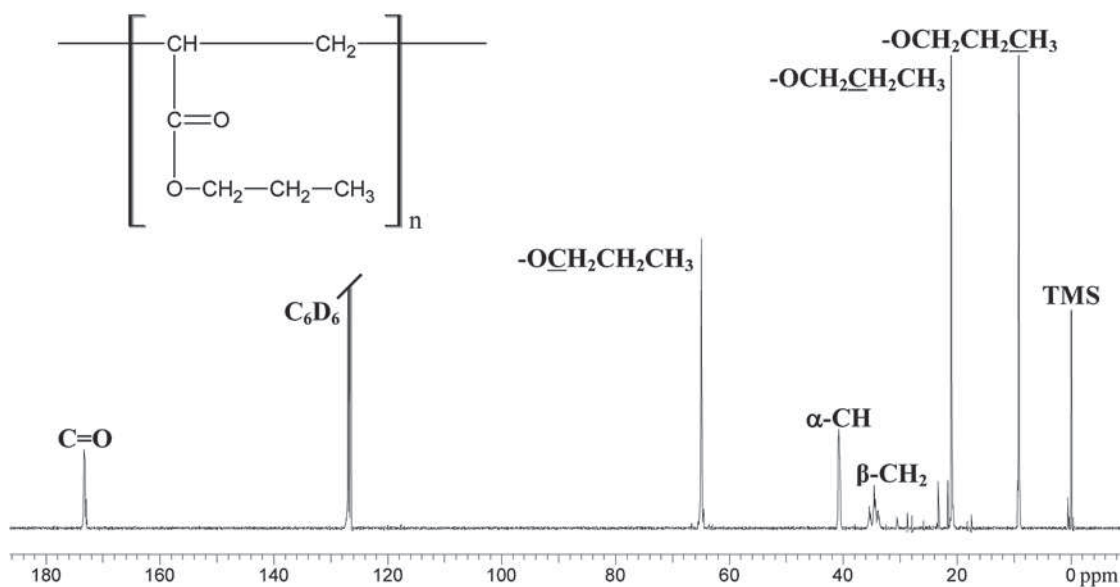


Figure 4. 100 MHz ^{13}C NMR spectrum of poly(*n*-propyl acrylate) recorded in C_6D_6

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 [2-4, 11-13, 15]. Table 1 shows the data necessary for simulation of the carbonyl signal PiPrA in C_6D_6 .

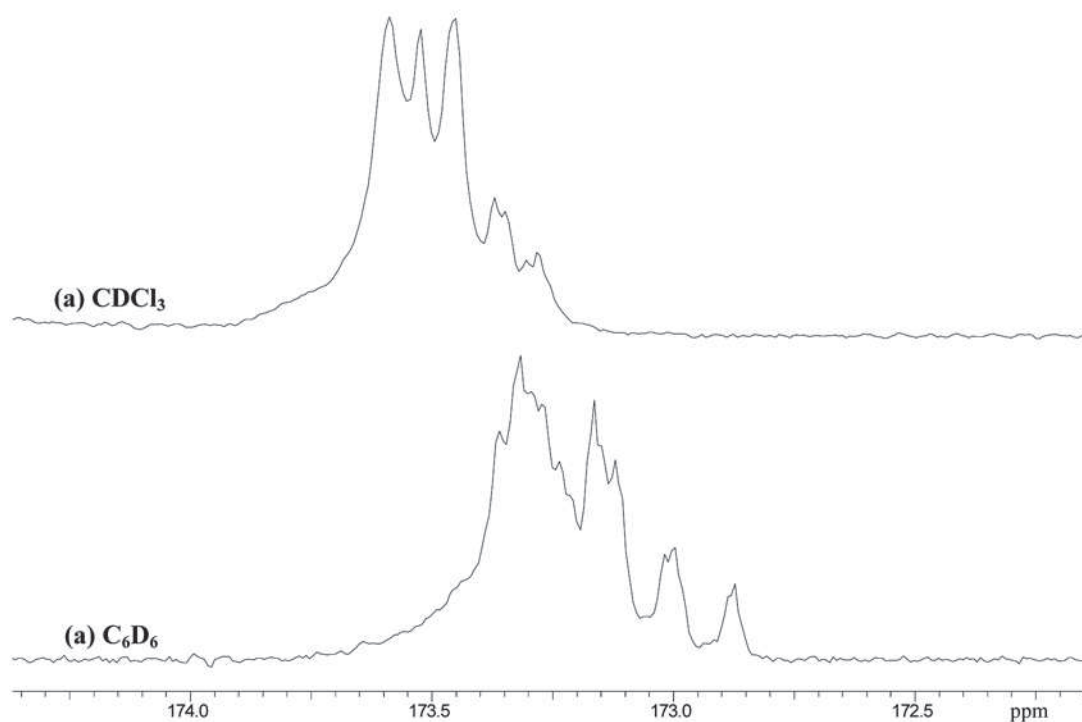


Figure 5. 100 MHz ^{13}C NMR carbonyl signal of poly(*n*-propyl acrylate) recorded in (a) CDCl_3 and (b) C_6D_6

Table 2 shows the data used to simulate the carbonyl signal of P*n*PrA at pentad level.

Table 2. Probabilities of configurational pentads of syndiotactic P*n*PrA calculated according to 1st order Markov statistics and chemical shifts calculated incrementally

Sequence	First-order Markov probabilities	Chemical shift, d [ppm]
P(<i>mmmm</i>)	0.002	172.92
P(\overline{mmmr})	0.013	172.90
P(<i>rmmr</i>)	0.027	172.88
P(\overline{mrmr})	0.015	173.07
P(\overline{mmrr})	0.052	173.14
P(\overline{rmmr})	0.063	173.05
P(<i>rmrr</i>)	0.220	173.12
P(<i>mrrm</i>)	0.030	173.22
P(\overline{rrrm})	0.211	173.29
P(<i>rrrr</i>)	0.368	173.36

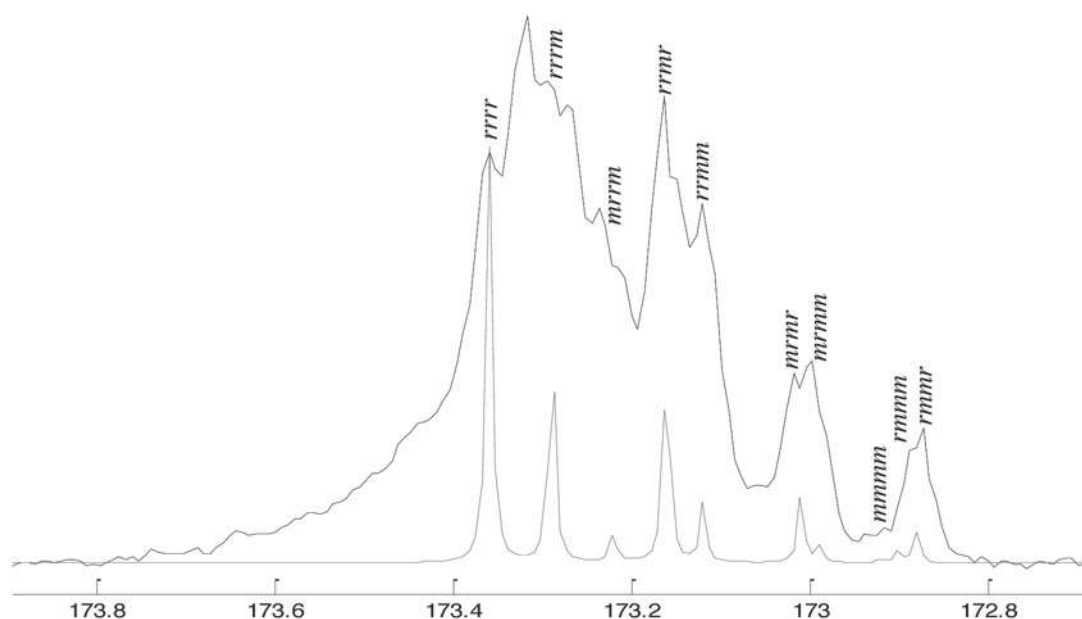


Figure 6. Simulation of the carbonyl signal of PnPrA in benzene- d_6 using 1st order Markov statistics and incremental calculation of chemical shifts at pentad level, linewidth 2 Hz

Simulation of the carbonyl signal of PnPrA and PiPrA applying the above incremental parameters leads to good match of the line positions.

Figure 3 shows the simulations of the carbonyl signal of poly(isopropyl acrylate) at heptad level with attribution of individual sequences.

General agreement between the experimental and simulated spectra can be regarded as a confirmation of the proposed sequence attribution. The carbonyl signal of poly(*n*-propyl acrylate), PnPrA

Figure 4 shows the ^{13}C NMR spectrum of *n*-propyl acrylate homopolymer recorded in benzene- d_6 as well as attribution of the polymer carbon signals.

The lines of carbonyl signal of PnPrA occupy the region from 172.75 to 174.00 ppm, and in both solvents used they offer visible splitting due to configurational effects (Figure 5).

Again, CDCl_3 , the standard solvent applied in the NMR measurements of acrylic systems offers lower signal resolution, therefore, also for PnPrA the microstructure analysis was performed for

the spectrum recorded in benzene- d_6 . The triad distribution for PnPrA can be determined from $-\text{OCH}_2-$ signal by simple integration [11-13, 15]. The values obtained, $P(rr)=0.6091$, $P(\overline{mr})=0.3495$ and $P(mm)=0.0414$, indicate predominantly syndiotactic chain of poly(*n*-propyl acrylate). 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 carbonyl signal. Again, also for this homopolymer, we will henceforth use the 1st Markov distribution of configuration sequences. For poly(*n*-propyl acrylate), experimental data allows simulation only at pentad level, even though traces of some additional lines due to longer sequences (heptads) are also visible.

Simulation of the carbonyl signal of poly(*n*-propyl acrylate) based on the above increment values gives the spectrum presented in Figure 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 C_6D_6 offer good resolution of their carbonyl signals to observe signals of configurational pentad and heptad, respectively. Based on the analysis of the carbonyl signal, confirmed by positive spectra simulation, the sequence distribution up to configurational heptad can be determined. It was shown that incremental calculation can be utilized to determine positions of individual pentads and heptads.

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