Stereochemical Characterization of Poly(pentyl acrylate) by One and Two Dimensional NMR Spectroscopy

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ABSTRACT: The stereochemical structures of poly(pentyl acrylate) (PPA) prepared by solution polymerization is studied by the combination of one and two dimensional NMR spectroscopy. The OCH₂, methine, methylene, and the carbonyl carbon resonances are assigned to triad, tetrad and pentad sequences respectively. The polymerization mechanism was studied using the carbonyl and OCH₂ resonances. It was found that homopolymerization followed Bernoullian statistics. The various configurational assignments in the aliphatic region were done with the help of inverse HETCOR, inverse HETCOR-TOCSY, homonuclear DQFCOSY experiments.

KEY WORDS Poly(pentyl acrylate) / 1D and 2D Nuclear Magnetic Resonance Spectroscopy / Stereochemical / Microstructure /

Homo and copolyacrylates are of great interest in many industrial applications because of their wide range of physical and chemical properties that can be covered by an appropriate choice of side groups and copolymer system. Poly(pentyl acrylate) (PPA) is used as a viscosity index improver because of large pendant group. The physical and chemical properties of these polymers are greatly influenced by the microstructure, which involves the monomer distribution in the polymer chain and stereochemical arrangement of various groups. Thus the determination of configurational sequence distribution appears to be important.¹ The knowledge of the microstructure is essential to study the polymerization mechanism.² NMR spectroscopy is probably the most efficient technique for characterization of the stereochemical structure of polymers.^{3,4} Many workers^{5–9} have reported the stereochemical structure of polyacrylates by conventional one dimensional NMR spectroscopy. The contribution of two dimensional nuclear magnetic resonance spectroscopy (2D NMR) to the study of homopolymer microstructure has been universally recognized.¹⁰ Recently, the microstructure of the polyacrylates were studied by the application of inverse HETCOR (heteronuclear correlation) and DQFCOSY NMR spectroscopies.^{11–13}

In this manuscript, we report the microstructure of PPA and the polymerization mechanism. The various carbon resonances are assigned to triad, tetrad and pentad configurational sequences with the help of two dimensional homonuclear (DQFCOSY) and heteronuclear (inverse HETCOR) correlation NMR spectroscopy. 2D ¹H–¹³C heteronuclear correlation was used to assign the proton NMR spectra of the homopolymers. The geminal and the vicinal couplings possible in the various configurational sequences in the homopolymer were studied by 2D ¹H–¹H DQFCOSY NMR spectroscopy.

EXPERIMENTAL

Pentyl acrylate was synthesized by esterification of pentanol with acrylic acid using the Dean and Stark apparatus. Benzene was used as azeotropic agent to remove the water from the reaction mixture. The monomer was vacuum distilled and stored below 5°C. The PPA was prepared by solution polymerization using benzoyl peroxide as initiator in DMF at 65°C. The homopolymer was precipitated in methanol and was reprecipitated using the CHCl₃/CH₃OH solvent system.

NMR experiments were performed in CDCl₃ on Bruker 300 MHz DPX spectrometer at a frequency of 300.13 MHz and 75.5 MHz for ¹H and ¹³C{¹H} NMR spectrum, respectively. DEPT measurements were carried in CDCl₃ using the standard pulse sequence with a *J* modulation time of 3.7 ms (*J*_{CH} = 135 Hz) with 2 s delay time. Two dimensional proton detected ¹H–¹³C heteronuclear chemical shift correlation and inverse HETCOR relay spectra were recorded in CDCl₃ using the standard pulse sequence.^{14,15} A total of 32 scans were accumulated with a relaxation delay of 2 s for each of the 512 *t*₁ experiments. The mixing time for the inverse HETCOR relay experiment was 6.4 ms. The DQFCOSY experiment, with 32 scans being collected for each *t*₁ value was carried out in CDCl₃. A total of 512 spectra each containing the 1 K data points were accumulated. The details of the Lorentzian shaped curve fitting have been described in our earlier publication.¹⁶ All regressions converged to $\chi^2 < 1$.

RESULTS AND DISCUSSION

The ¹³C{¹H} NMR spectrum of the PPA in CDCl₃ is shown in Figure 1. The various carbon resonance signal were assigned with the help of DEPT-135 experiment. Figure 2 shows the DEPT-135 NMR spectrum of the homopolymer in which the methylene carbon resonances have negative phase and the methine and the methyl carbon resonances show positive signals. The alkyl side chain methylene carbons show signal around δ 63.68,

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The ^{13}C NMR spectrum of 1,4-dioxane shows several characteristic peaks. The x-axis represents the chemical shift in ppm, ranging from approximately 10 to 65. The spectrum includes the following labeled peaks:

- OCH₂**: A sharp peak at approximately 64 ppm, corresponding to the carbons bonded to oxygen.
- CH**: A sharp peak at approximately 41 ppm, corresponding to the methine carbons.
- CH₂**: A complex multiplet between 33 and 37 ppm, corresponding to the methylene carbons in the ring.
- CH₂**: A sharp peak at approximately 28 ppm, corresponding to the methylene carbons.
- CH₂**: A sharp peak at approximately 23 ppm, corresponding to the methylene carbons.
- CH₂**: A sharp peak at approximately 18 ppm, corresponding to the methylene carbons.
- CH₃**: A sharp peak at approximately 14 ppm, corresponding to the methyl carbons.

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δ 28.24, δ 27.94, and δ 22.46 ppm which are assigned to $-\text{OCH}_2$, $^2\text{CH}_2$, $^3\text{CH}_2$, and $^4\text{CH}_2$. The side chain methyl carbon resonances around δ 13.93 ppm. The β -methylene and the methine carbon signals shows multiplets around δ 33.0–36.0 and δ 40.0–40.75 ppm, respectively. The OCH_2 carbon signals show three multiplet around δ 63.4–63.65, δ 63.65–63.76, and δ 63.76–64.0 ppm, which are assigned to *rr*, *rm/mr*, and *mm* from high to low field. The triad concentration were calculated from the area under these signals. From these triad fractions, using the Bernoullian statistics,³ the probability of *meso* addition to the growing polymer chain (*P_m*) was calculated. The average value of *P_m* from the triad fractions is 0.425. Using the triad concentration data, one can test whether the propagation reaction obeys Bernoullian statistics. The probability that the monomer unit added to a growing polymer chain terminated by a racemic diad will generate a *meso* diad (*P_{r/m}*) is given by the relation³

$$P_{r/m} = \frac{mr}{2rr + mr}$$

and similarly for *P_{m/r}*

$$P_{m/r} = \frac{mr}{2mm + mr}$$

when *P_{r/m}* + *P_{m/r}* = 1, then chain propagation obeys Bernoullian statistics. For PPA, the sum of the *P_{r/m}* and *P_{m/r}* equals 0.95, which approximate to 1 within ex-

Table 1. The experimentally and statistically determined triad fractions of various carbon resonances

Triads	Triad fractions				
	Theoretical ^a	$-\text{OCH}_2$ ^b	Carbonyl ^b	Methine ^b	Methylene ^b
<i>mm</i>	0.18	0.21	0.21	0.17	
<i>mr(rm)</i>	0.49	0.47	0.47	0.83 ^c	
<i>rr</i>	0.33	0.32	0.32		
<i>mmm</i>	0.08				0.12
<i>rmm</i>	0.21				0.20
<i>rmr</i>	0.14				0.08
<i>mrmm</i>	0.10				0.13
<i>rrm</i>	0.28				0.27
<i>rrr</i>	0.19				0.19
<i>mmmm</i>	0.03		0.02		
<i>mmmr</i>	0.09		0.10		
<i>rmmr</i>	0.06		0.09		
<i>mmrm</i>					
+	0.21		0.19		
<i>mmrr</i>					
<i>rmrm</i>	0.12		0.10		
<i>rmrr</i>	0.16		0.18		
<i>mrrm</i>					
+	0.22		0.19		
<i>mrrr</i>					
<i>rrrr</i>	0.11		0.13		

^a Calculated from Bernoullian Statistics using *P_m* = 0.425. ^b Determined from $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. ^c The triad concentration of 0.83 is inclusive of *mr(rm)* + *rr*.

Figure 3. The 300 MHz ^1H - ^{13}C proton detected heteronuclear shift correlation spectrum of PPA.

Figure 4. The inverse HETCOR spectrum of PPA, showing the methine and the methylene correlation cross peaks.

perimental error, thus the polymerization obeys Bernoullian statistics. This Pm value was used to calculate the triad, tetrad and pentad sequences concentration in the homopolymer.

The signals around δ 174.0–174.7 ppm are assigned to the carbonyl carbon resonances. The signals around δ 174.0–174.35, δ 174.35–174.52, and δ 174.52–174.7 ppm are assigned to mm , mr/rm , and rr triads. The further splitting within these triad fractions can be assigned to pentad sequences (Figure 1). Therefore the signals at δ 174.11, δ 174.25, and δ 174.3 ppm are assigned to $mmmm$, $mmmr$ ($rmmm$), and $mmrm$ pentad sequences. In the mr triad fraction region the signals at δ 174.41, δ 174.6, and δ 174.5 ppm are assigned to $mmrm + mmrr$, $rmrm$, and $rmrr$ pentads. The $rrrr$ and $mrrm + mrrr$ pentads are assigned at δ 174.57 and δ 174.53 ppm, respectively. These assignments are based on the assignments done by Bovey *et al.*³ for poly(methyl methacrylate) (PMMA). These assignments are also confirmed by calculating the area under these signals and comparing them with those calculated using the Bernoullian statistics ($Pm = 0.425$). There was good agreement between the experimentally and statistically determined triad and pentad fractions (Table I).

The methine carbon signal also shows triad configurational sensitivity. The mm triad fraction which appears at higher field (δ 40.18 ppm) whereas the mr and rr triad fractions are not distinguishable and appears at δ 40.34 ppm. The β -methylene carbon resonance signal shows tetrad sensitivity which were assigned with the

help of the 2D inverse-HETCOR as demonstrated by Suchoparek *et al.*¹¹ Figure 3 shows the inverse-HETCOR NMR spectrum of PPA. The m centered tetrads (mmm , mmr , and rmr) have non-equivalent methylene protons, thus will show two crosspeaks in the F2 domain of the 2D spectrum (Figure 4) whereas the r centered tetrads (mrm , mrr , and rrr) will show one correlation crosspeak. Roman *et al.*¹ showed that the chemical shift of the m centered tetrads increases in the order mmm , mmr , and rmr . Thus the correlation cross peaks at δ 33.36/1.51 (δ 33.36/1.88), δ 34.19/1.46 (δ 34.19/1.89), and δ 35.23/1.41 (δ 35.23/1.91) ppm are assigned to mmm , mmr , and rmr tetrads. The r centered tetrads are assigned at δ 35.39/1.61 (rrr), δ 34.32/1.62 (mrr), and δ 33.74/1.64 (mrm) ppm. The area under these tetrad fraction were calculated from the methylene region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The expanded methylene and methine carbon resonances are shown in Figure 5. These tetrad fraction were then compared with those found out using the Bernoullian statistical model (Table I). There is good agreement between the experimentally determined and statistically determined tetrad fractions, thus confirming the assignments.

Figure 6 shows the ^1H - ^{13}C heteronuclear relay (through HOHAHA) spectrum of PPA in CDCl_3 . In the spectrum apart from the correlation crosspeaks, relayed coupling by magnetization transfer through spin system are also observed. The long range relay coupling will be seen at longer mixing time whereas the direct couplings will be seen at shorter mixing time. The directly

Figure 5. The expanded $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of PPA showing the methine and the β -methylene carbon resonances.

Figure 6. The inverse HETCOR relay (through spin lock) correlation spectrum, (a) the complete spectrum, (b) the expanded portion showing the methine and the methylene regions, of PPA.

correlating β -methylene crosspeaks are marked on the basis of the above assignment. The corresponding relay peaks, arising from the magnetization transfer from CH_2 protons to the neighbouring CH proton confirms the above assignments. The methylene protons in *rrr*, *mrm*, *rmr*, and *mmm* tetrads will give relay peaks to *rr*, *mr*, and *mm* methine protons. The *mrr* and *mmr* methylene proton will show relay peaks with *mr*, *rr* and *mm*, *mr* methine protons.

From the heteronuclear correlation spectroscopy the ^1H NMR spectrum is completely assigned. Figure 7 shows the ^1H NMR spectrum of PPA in CDCl_3 . The methine protons at $\delta 2.27$ and $\delta 2.32$ ppm are assigned

to *mm* and *mr+rr* triad fractions. The geminal coupling of the non equivalent methylene proton in the *m* centered tetrads are clearly seen in the COSY spectrum (Figure 8). The cross peaks at $\delta 1.1.91/1.41$, $1.89/1.46$, and $1.88/1.51$ ppm are due to the geminal couplings of the methylene protons in *rmr*, *mmr*, and *mmm* tetrads. The coupling between the methine proton with the two different methylene protons in the *mm* triad fraction are at $\delta 2.34/1.88$ and $\delta 2.34/1.49$ ppm. Similarly, the CH/CH_2 couplings in the *mr* triad fraction are at $\delta 2.29/1.91$ and $\delta 2.29/1.43$ ppm. Due to the cancellation of the crosspeaks in the DQFCOSY spectrum, these cross peaks are clearly seen in the low mixing

Figure 7. The 300 MHz ^1H NMR spectrum of PPA in CDCl_3 .

Figure 8. The homonuclear 2D DQFCOSY spectrum of PPA in CDCl_3 , (a) complete spectrum, (b) expanded region showing the methine/methylene couplings.

time TOCSY (4 ms) spectrum.

CONCLUSIONS

The microstructure of the PPA was determined with the help of $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. The polymerization mechanism was found to obey Bernoullian statistics. There was good agreement between the experimentally and statistically determined triad, tetrad,

and pentad fractions. The various configurational assignments of the carbon and proton resonances were done with the help of both homonuclear (DQFCOSY) and heteronuclear (inverse HETCOR and inverse HETCOR-relay) correlation NMR spectroscopy.

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