PII: S0032-3861(96)00908-1

Polymer Vol. 38 No. 14, pp. 3625–3635, 1997
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0032-3861/97/$17.00 + 0.00

Microstructural analysis of poly(4-N-acrylamide-2-hydroxybenzoic acid) and poly(5-N-acrylamide-2-hydroxybenzoic acid) by ^{13}C n.m.r. spectroscopy

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(Received 30 July 1996; revised 23 September 1996)

The microstructural analysis of both poly(4-N-acrylamide-2-hydroxybenzoic acid) (poly(4-AHA)) and poly(5-N-acrylamide-2-hydroxybenzoic acid) (poly(5-AHA)) was carried out by one-dimensional ^{13}C n.m.r. spectroscopy. The sensitivity of aromatic carbon signals to the stereosequences was found to depend mainly upon the carbon ability to extend into the maximum shielding zone of the neighbouring phenyl rings and carboxyl oxygens. The sensitivity of the amide carbonyl signal to the chain microstructure is influenced mainly by the γ-*gauche* shielding effect. Solvent-induced effects in the spectra of poly-(4-AHA) are rationalized in terms of H-bonds (for aromatic carbon signals) and bond conformation changes (for amide carbonyl carbon signal). The increase of amide carbonyl carbon signal sensitivity to the stereosequences in the spectrum of poly(5-AHA) in comparison with that of poly(4-AHA) reflects the conformation changes, induced by the transfer to more sterically crowded polyacrylate. For both poly(4-AHA) and poly(5-AHA) prepared by radical polymerization the Bernoullian statistics is required to fit the observed intensities at the triad and pentad level. © 1997 Elsevier Science Ltd.

(Keywords: n.m.r. spectroscopy; stereochemistry; substituted poly(acrylamides))

INTRODUCTION

The polymers containing salicylic acid residues are known for their biological activity[1-3] and also for applications to ion-exchange chomatography of cationic materials and selective binding of positively charged molecules to form insolubilized derivatives of enzymes, proteins and glycoproteins including immunoglobulins[4,5].

The chemical and physical properties of these polymers seem to be influenced fundamentally by the microstructure of the polymer chains and therefore the determination of configuration sequence distribution appears to be important. Probably, the most classical example is the excellent mechanical properties of isotactic polypropylene in comparison with those of the atactic and syndiotactic polymer as a consequence of the tridimensional order of the isotactic sequences[6,7]. Poly(acrylonitrile) is another good example because of the repulsive or attractive interactions of the side nitrile groups according to their relative spatial orientation, which facilitates the formation of acrylic fibres with excellent mechanical properties after the adequate drawing process[8]. Moreover, the reactivity of active side groups in high molecular weight polymeric chains is strongly affected by the stereochemical configuration of the monomeric repeating units in such a way that the side groups of *meso* or *racemic* dyads or in general those of isotactic and syndiotactic sequences participate in specific chemical or thermal reactions selectively[9].

Different polyacrylates have been the subject of many n.m.r. studies both by ^{1}H$^{10-12}$ and ^{13}C$^{13-17}$ n.m.r. spectroscopy. The latter has become the method of choice (due to its greater sensitivity to structural detail) for investigating the stereochemical structure of polyacrylates with aromatic ring as a side chain[18,19], but the stereochemistry of polymers containing salicylic acid residues have not been studied before.

The goal of the present work was to carry out the detailed microstructural analysis of poly(4-AHA) and poly(5-AHA) holding potential for applications in industry and medicine by means of the high frequency n.m.r. spectrometer, enabling us to study the polymer chain tacticity using not only backbone and carbonyl but also aromatic carbon signals.

EXPERIMENTAL

Monomers

4-N-Acrylamido-2-hydroxybenzoic acid (4-AHA) was prepared by analogy with the method of Kennedy[20]

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[0.13 mol of 4-amino-2-hydroxybenzoic acid was dissolved in a mixture of aqueous HONa (5%), dioxane (200 ml) (volume ratio 4/1) and triethylamine (27.6 ml)]. Two separate additions of acryloyl chloride (10 and 5.84 ml, 0.195 mol) were made to the solutions being stirred for 1 h after each addition. After 3 h reaction dioxane was distilled off at reduced pressure and to the remaining HONa aqueous solutions dilute HCl was added to precipitate 4-AHA which was recrystallized twice from methanol/water (2/1). The yield of 4-AHA amounted to about 60%, melting point (m.p.) was found to be 230°C.

5-N-Acrylamide-2-hydroxybenzoic acid (5-AHA) was prepared in a similar way as 4-AHA, but using 5-amino-2-hydroxybenzoic acid. The yield amounted to about 50%, m.p. was found to be 220°C.

Polymers

Poly(4-N-acrylamido-2-hydroxybenzoic acid) (poly(4-AHA)). 4-AHA was polymerized by free radical polymerization in dimethylformamide (DMF) solution at 50°C in a thermostatic bath under oxygen-free N_2. 2,2'-Azobisisobutyronitrile (AIBN) was used as initiator, $[I] = 1.5 \times 10^{-2}\,\mathrm{mol\,l^{-1}}$. After 10 h the reaction mixtures were added to a large excess of ethyl ether. The precipitated polymer was filtered off and vacuum dried over P_2O_5 to constant weight. The yield of the polymer product amounted to about 80%. The number-average molecular weight (M_n) determined by s.e.c. (using DMF and PSt standards) was found to be 55 000 with polydispersity index (M_w/M_n) being 1.5.

Poly(5-N-acrylamido-2-hydroxybenzoic acid) (poly (5-AHA)). 5-AHA was polymerized by analogy with 4-AHA. The yield of the polymer product amounted to about 75%. The value of M_n determined by s.e.c. was 58 000 with M_w/M_n being 1.42.

N.m.r. measurements

^{13}C n.m.r. spectra of polymers poly(4-AHA) and poly(5-AHA) were recorded on a Varian XL-300 spectrometer (operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C n.m.r.) and on a Varian Unity-500 spectrometer (operating at 499 MHz for ^{1}H and 125.7 MHz for ^{13}C n.m.r.) at 70°C using 10% (w/v) solutions of poly(4-AHA) in D_2O and DMSO-d_6 and solutions of poly(5-AHA) in DMSO-d_6. The intensity of signals was measured by electronic integration, deconvolution or when was necessary by triangulation and planimetry of expanded spectra. All chemical shifts are referred to hexamethyldisiloxane.

Theoretical calculations

Semiempirical calculations of the electron density of the aromatic carbons C-4 to C-9, were made by using the original parameters of the programme AM1[21], based on the restricted Hartree–Fock (RHF) method, included in MOPAC version 6.0[22]. This semiempirical method appears to allow a better description of the hydrogen bonds in many organic compounds[23–25]. The program ran on an ALPHA 2100 computer of the Computer Centre of CSIC (Madrid, Spain).

Initial geometries determining the distance *D* between the aromatic carbons and the carbonyl oxygen of the neighbouring units, were obtained by molecular mechanics (MM+) by means of the program Hyperchem version 4.5[26]. The results of this optimization were employed as input data for the semiempirical calculations. The same program was used to visualize the structures obtained after MOPAC minimization. Geometries were optimized in internal coordinates. The optimization was stopped when Herbert or Peter tests were satisfied in the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method[27]. The PRECISE option was applied during the optimization process with the gradient norm set to 0.01. The calculations were carried out with full geometry optimization (bond lengths, bond angles and dihedral angles). As a starting point the classical parameters for polymethacrylic chains suggested by Vacatello and Flory[28] and Tonelli[29] were considered, i.e. valence angles at the quaternary carbon $CH_2{-}C{-}CH_2 = 106°$, *111°* and *116°* when both attached backbone bonds are *trans*, when one is *trans* and the other is *gauche*, and when both are *gauche*, respectively. In addition, the approximation of the most probable *trans* configuration for polymer sequences was also taken into consideration to enter the program. Mulliken population analyses[30] used to discuss the electron distributions are adequate for the present purpose since they reflect the trends in populations and charges which seem to be important rather than their actual values. Values of π-bond electronic density and π-bond order were computed by using the P1 and Mullik options of the MOPAC 6.0 program. The values of ESP (electrostatic potential charges) were calculated with ESP option.

The molecular models of the lowest energy for mm-triad sequence in the polymer chains of poly(4-AHA) and poly(5-AHA) were built up using the analogous computer program.

RESULTS AND DISCUSSION

Poly(4-AHA) spectra

Aromatic carbon region. The 125 MHz ^{13}C n.m.r. spectrum of poly(4-AHA) in DMSO-d_6 solution is presented in *Figure 1*. The assignment of the signals was made on the basis of additive scheme calculations[31] and by comparison with the spectrum recorded using DEPT sequence[32]. In this spectrum one can observe the splitting of only two aromatic carbons (**C-7** and **C-8**) proved to be microstructure sensitive.

The sensitivity of side chain carbon signals to the polymer stereoregularity appears to arise from at least two factors: γ-*gauche* effect and the influence of the neighbouring side-chain substituents[33]. However, the aromatic carbons of a substituted phenyl ring are not sensitive to the γ-*gauche* effect because of the rigidity and electronic conjugation of the aromatic ring[33]. This concept is also applicable to the possible influence of the long range interactions between the carbon atom C-4 and the methine group of the backbone acrylic chain[34,35]. Therefore, it can be considered that the specific influence of the neighbouring side substituents on the chemical shift of aromatic carbons of the central unit is the main source of the observed chemical shift dispersion among the various stereosequences. In this sense, it is clear from *Figure 2* that the ^{13}C n.m.r. spectrum of poly(4-N-methacrylamide-2-hydroxybenzoic acid) (poly(4-Me-AHA)) presents all the aromatic carbons (including **C-7** and **C-8**) as single peaks, insensitive to the polymer

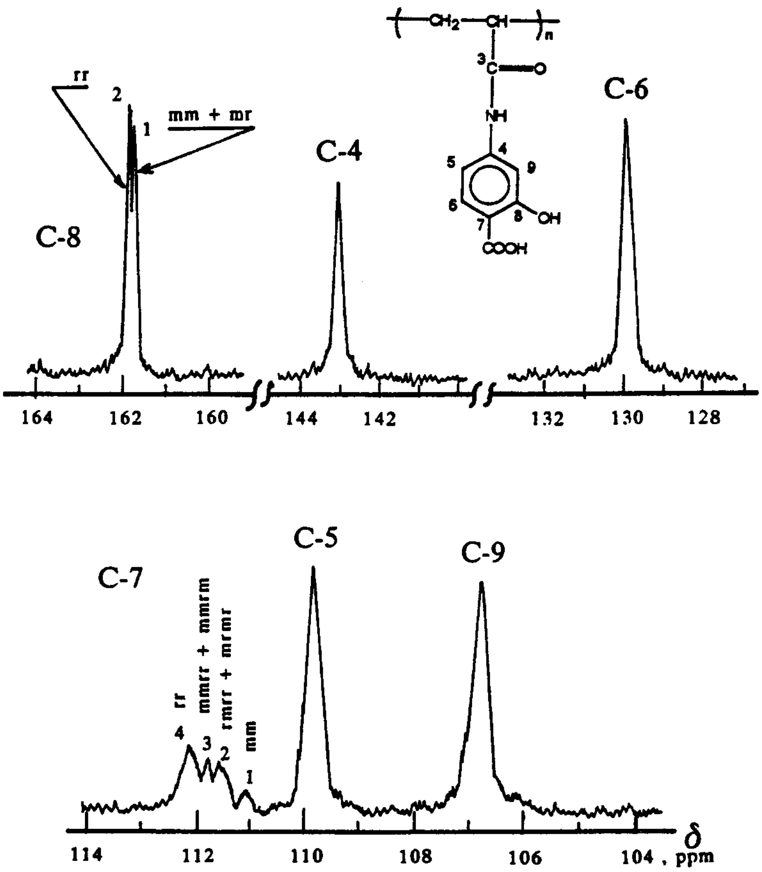

Figure 1 ^{13}C n.m.r. spectrum (125.7 MHz) of poly(4-AHA) (the aromatic carbon region) recorded in DMSO-d_6 at 70°C

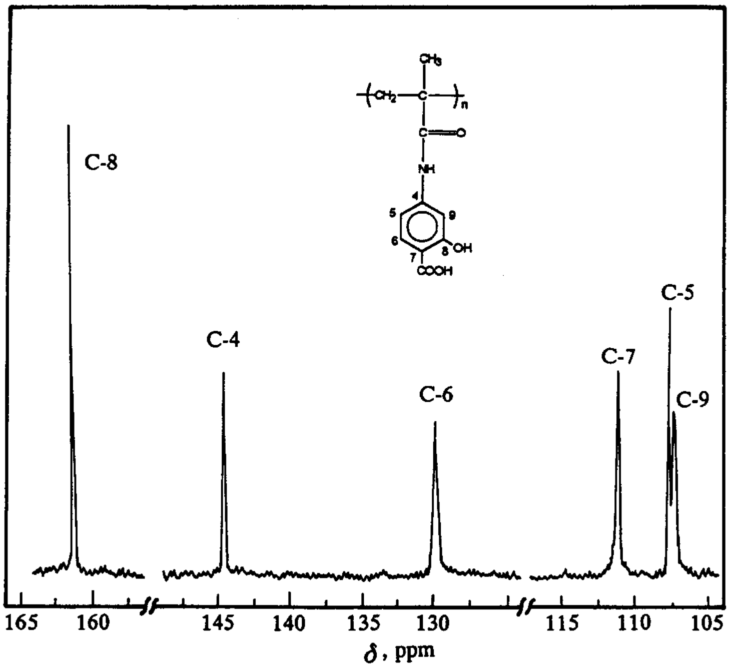

Figure 2 ^{13}C n.m.r. spectrum (75 MHz) of poly(4-Me-AHA) (the aromatic carbon region) recorded in DMSO-d_6 at 70°C

stereoregularity, which provides the support for this assumption. Actually, since this disubstituted vinyl polymer is known to be sterically crowded the backbone valence angle $\angle C{-}CH_2{-}C$ is expanded some 15° from the normal tetrahedral value[29], resulting in a reduction in the influence of the side chain substituent, which is considered to be the sole source of the aromatic carbon sensitivity to the stereosequences.

This observation probably reflects the fact that ring currents from neighbouring phenyl rings make only a modest contribution to the shielding at the aromatic carbons of the central unit (C^*_{arom}), while carboxylic

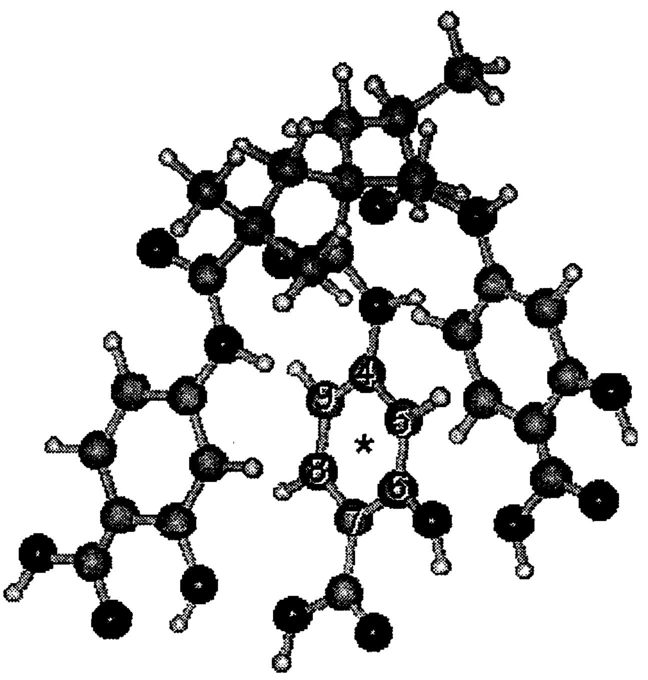

Figure 3 Molecular model of the lowest energy for mm-triad (in all *trans* planar zigzag conformation) in the chain of poly(4-AHA). Central aromatic ring is marked by *

Table 1 The average space distance (D) between C^*_{arom} and acid carbonyl oxygens of the first neighbouring phenyl groups and the comparative analysis of aromatic carbon signal sensitivity to stereosequences in the polymer chain of poly(4-AHA)

Aromatic carbon	Electron density[a]	D, Å[b]	Overall spread of carbon chemical shifts $\Delta\sigma$, ppm[c]
C-7	4.25	4.81	< 1.0
C-9	4.26	5.70	0.70
C-5	4.22	5.61	0.35
C-6	4.01	5.78	0.45
C-4	3.84	6.98	0.10
C-8	3.80	5.14	0.12

[a] Mulliken electron densities calculated by MOPAC version 6.0[22]
[b] Measured in the molecular model of the mm-triad in the poly(4-AHA) chain (*Figure 3*) by the computer program Hyperchem version 4.5[26]
[c] In the spectrum presented in *Figure 4* (solvent: D_2O)

oxygens of COOH groups linked to neighbouring phenyl rings produce greater shielding effect but only at those C^*_{arom} which can extend into the shielding zone[36] of the carboxylic oxygen. This suggestion is consistent with the fact that the aromatic ring is characterized by the lack of the π-bond electronic density (1.07) known to determine the value of diamagnetic shielding effect[31,37], whereas the carboxylic oxygen (π bond C=O is polarized toward oxygen[31]) is characterized by the excess of π-electron density (0.26). The support for this suggestion also is provided by the values of the average spatial distance (D) between C^*_{arom} and carboxylic oxygens of the first neighbouring phenyl rings measured in the molecular model of the mm-triad (*Figure 3*). Actually, values of D collected in *Table 1* show that **C-7** and **C-8** carbons of the central unit are arranged in the space closer to the neighbouring carboxylic oxygens than other aromatic carbons. However, it is necessary to keep in mind that the π-electron cloud does not have its maximum electron density (and as a consequence its maximum shielding effect) at the carboxylic oxygen but exists rather in two doughnut-like rings with the spacing of the order of 1 Å[37].

It is worth noting that in the 125.7 MHz ^{13}C n.m.r. spectrum of poly(4-AHA) recorded in D_2O solution (*Figure 4*) aromatic carbon signals **C-4**, **C-5**, **C-6** and **C-9** proved to be more sensitive while aromatic signals **C-7** and **C-8** were slightly less sensitive to the polymer stereoregularity than those of the spectrum recorded in DMSO-d_6 (*Figure 1*). This observation can be explained in terms of H-bonds between water molecules and carboxylic oxygens which appear to be sterically accessible to the solvent (*Figure 3*). Apparently, polar solvents can disrupt a planar six-membered cycle which is formed by the internal association of the HO and COOH groups in *ortho*-position[25,33] (*Figure 3*). The formation of these H-bonds probably leads to the following changes:

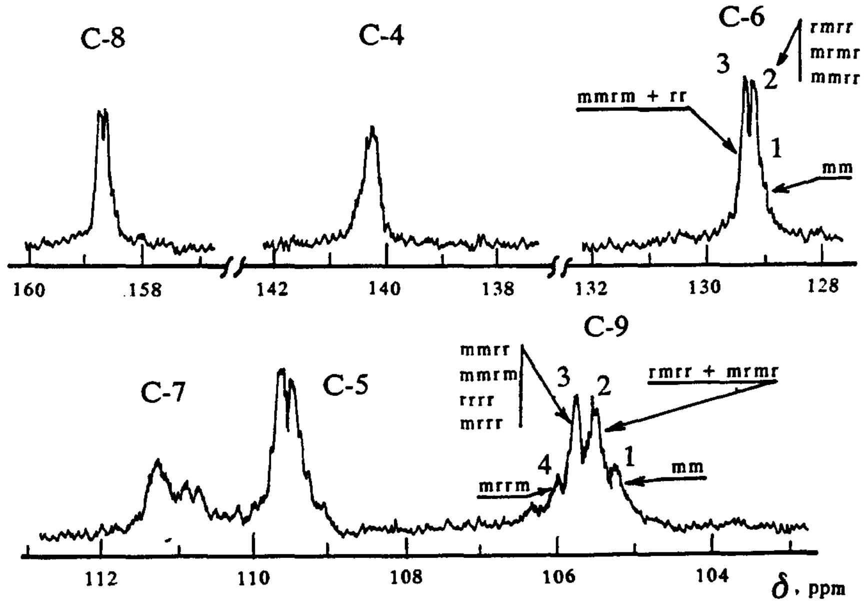

Figure 4 ^{13}C n.m.r. spectrum (125.7 MHz) of poly(4-AHA) (the aromatic carbon region) recorded in D_2O at 70°C

Table 2 Assignment of the ^{13}C n.m.r. resonance signals of the aromatic carbons for triad and pentad sequences of poly(4-AHA) chains

Aromatic carbon	Peak number	Integration limits in ^{13}C n.m.r. δ, ppm	Sequence	Molar ratio	
				Experimental	Calculated[c]
C-6[a]	1	128.8–129.0	mm	0.13	0.14
	2	129.0–129.3	rmrr		0.18
			mrmr	0.40	0.11
			mmrr		0.11
	3	129.3–129.9	mmrm	0.46	0.06
			rr		0.40
C-9[a]	1	105.0–105.3	mm	0.15	0.14
	2	105.3–105.6	rmrr	0.29	0.18
			mrmr		0.11
	3		mmrr		0.11
		105.6–105.9	mmrr	0.47	0.06
			rrrr		0.16
			mrrr		0.18
	4	105.9–106.2	mrrm	0.09	0.06
C-8[b]	1	161.3–161.8	mm	0.59	0.14
			mr		0.46
	2	161.8–162.1	rr	0.43	0.40
C-7[b]	1	110.8–111.2	mm	0.10	0.14
	2	111.2–111.7	rmrr	0.30	0.18
			mrmr		0.11
	3	111.7–111.9	mmrr	0.16	0.11
			mmrm		0.06
	4	111.9–112.5	rr	0.44	0.40

[a] Spectrum presented in *Figure 4*
[b] Spectrum presented in *Figure 1*
[c] According to Bernoullian statistics ($P_m = 0.37$; $P_r = 0.63$)

(a) carboxylic oxygens appear to be blocked by water molecules that results in reducing their shielding effect produced at **C-7** and **C-8** carbons of the central unit;

(b) neighbouring phenyl group prove to be highly associated with the phenyl ring of the central unit that seems to result in the intensification of its ring current shielding effect produced at C^*_{arom}. This spatial factor seems to be prevalent by taking into account that the total π-bond electronic density of the aromatic ring only increased slightly (4.95).

Thus, the comparison of spectra shown in *Figures 1* and *4* enables us to draw the following conclusion: in the spectrum recorded in D_2O aromatic carbon signals of the central unit are mainly influenced by the ring current effect of the neighbouring phenyl rings, whereas in the spectrum recorded in DMSO-d_6 they are affected by the shielding effect of the carboxylic oxygens of COOH-groups linked to the neighbouring phenyl rings.

In the spectrum presented in *Figure 4* signals of aromatic carbons **C-6** and **C-9** proved to be the most informative ones upon the polymer chain microstructure: signal **C-9** is observed in an interval of $\Delta\delta = 0.70$ ppm (105.20–105.90 ppm) and splits into four peaks due to pentad sequences; signal **C-6** is observed in an interval of $\Delta\delta = 0.45$ ppm (128.90–129.35 ppm) and splits into three peaks due to triad and pentad sequences. In the spectrum presented in *Figure 1* signals of aromatic carbon **C-8** and **C-7** provide the information on the polymer chain stereoregularity at triad and pentad level, respectively: signal **C-8** is observed in an interval of $\Delta\delta = 0.11$ ppm (161.74–161.85 ppm) and splits into two peaks, while signal **C-7** is observed in an interval of $\Delta\delta = 1.07$ ppm (111.08–112.15 ppm) and splits into four peaks.

In pentad sequences aromatic carbons of the phenyl ring of the central unit ($\mathbf{R}^*$) are influenced both by the first neighbour groups ($\mathbf{R}^\alpha$) and by the second neighbour groups in the terminal dyads of the pentad structure ($\mathbf{R}_1^\beta$, $\mathbf{R}_2^\beta$) which have the same configurational arrangement as $\mathbf{R}^*$ (*Figure 3*). By analogy with the data of Tonelli[33] both $\mathbf{R}^\alpha$ and $\mathbf{R}_1^\beta$ produce shielding while $\mathbf{R}_2^\beta$ deshielding effect at the $\mathbf{R}^*$ (C^*_{arom}). Keeping it in mind we have tentatively assigned the low field component of the **C-9** carbon signal (peak 4, *Figure 4*) to **mrrm** pentad in which $\mathbf{R}^\alpha$ and $\mathbf{R}_1^\beta$ are remote from $\mathbf{R}^*$ (*Figure 3*). The Bernoullian probabilities P_m and P_r (being 0.37 and 0.63, respectively) were obtained from the experimental estimate (using the relative intensity of the peak 4) of the **mrrm** pentad content. The complete signal assignment in both spectra was made (*Table 2*) on the basis of similar data reported by Tonelli[33], and by a comparison of experimental signal intensities with calculated pentad population assuming Bernoullian trial[39].

It should be interesting to carry out the comparative analysis of the sensitivity of different aromatic carbon signals to sequences in the spectrum of poly(4-AHA),

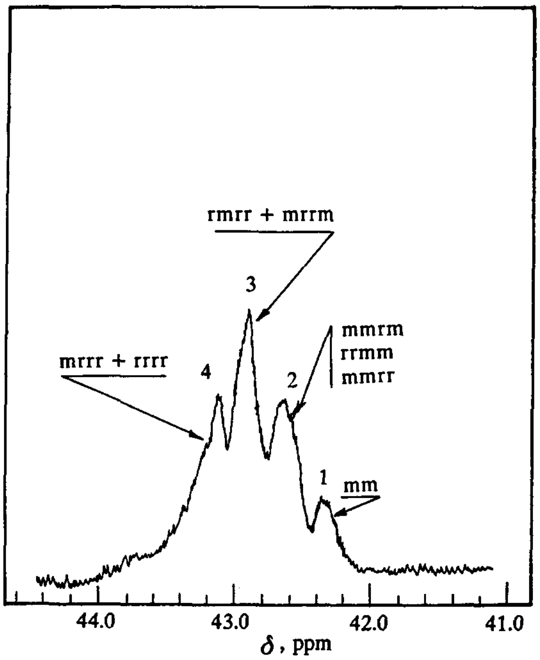

Figure 5 ^{13}C n.m.r. spectrum (125.7 MHz) of poly(4-AHA) (the main chain CH carbon region) recorded in D_2O at 70°C

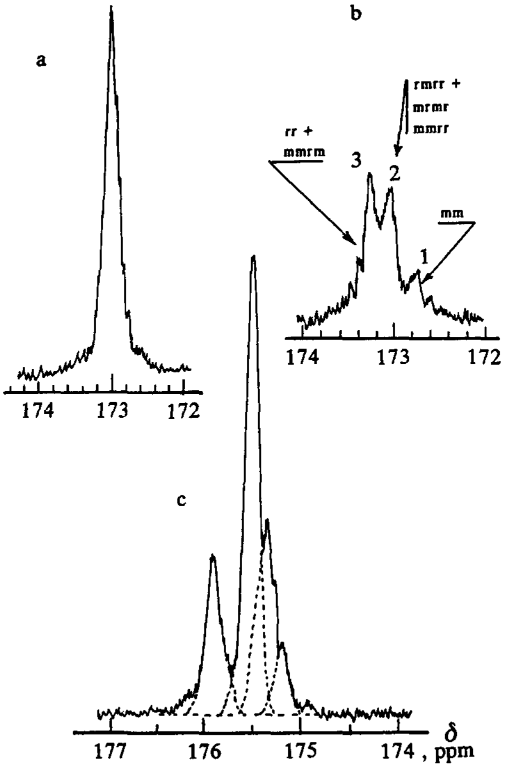

Figure 6 125.7 MHz (for poly(4-AHA)) and 75 MHz (for poly(4-Me-AHA)) ^{13}C n.m.r. spectra (the amide carbonyl carbon region) recorded at 70°C: solutions of poly(4-AHA) in DMSO-d_6 (a) and D_2O (b); solution of poly(4-Me-AHA) in DMSO-d_6 (c)

recorded in D_2O bearing in mind that these signals are influenced by ring current shielding. The effect produced by ring currents appear to depend on both the spatial vicinity of the carbon to the shielding zone[36] and the carbon electron density whose decrease seems to result in the increasing of the carbon sensitivity to the shielding[31]. Data collected in *Table 1* clearly show that the order of the carbon electronic density decreasing **C-7** $\approx$ **C-9** > **C-5** > **C-6** > **C-4** > **C-8** does not correlate with the order of carbon sensitivity increasing (overall spread of carbon chemical shifts) **C-4** < **C-8** < **C-5** < **C-6** < **C-9** < **C-7**. This trend is probably due to the fact that carbons **C-5**, **C-6**, **C-7** and **C-9** can approach (to more or less extent) to the shielding zone of ring currents, while carbons **C-8** and **C-4** appear to be on the periphery of this zone. At any rate the spatial factor proves to be overriding.

Methine carbon region. The main chain CH-signals appear in an interval of $\Delta\delta = 0.82$ ppm (42.3–43.12 ppm) and split into four peaks due to pentad sequences (*Figure 5*).

Unlike aromatic carbons the backbone methine carbon exhibits ^{13}C chemical shifts mainly influenced by the γ-*gauche* effect, according to which the CH-group of the pentad central unit (CH*) is experiencing γ-*gauche* shielding effects produced both by γ-substituent CH_2 with conformation bond probability P_g and γ-substituent $C(O)NHC_6H_3(COOH)(OH)$ with conformation bond probability P_t[33]. The chemical shift of the CH*-group appears to be sensitive to long-range interactions[34]: so the CH_2-groups in α-(CH_2^{α}) and CH-groups in β-position (CH^{β}) to CH* are also influenced by γ-*gauche* shielding effects. These shielding *g*-1.4 interactions should reduce the deshielding effects[31] produced by the CH_2^{α} and CH^{β} groups at CH* (*g*-1.5 and *g*-1.6 interactions respectively).

Table 3 Assignment of the ^{13}C n.m.r. resonance signals of the main chain CH-group for pentad sequences of poly(4-AHA) chains

Peak number	Integration limits in ^{13}C n.m.r. δ, ppm	Sequence	Molar ratio Experimental	Molar ratio Calculated[a]
1	42.0–42.4	mm	0.10	0.14
2	42.4–42.7	mmrm		0.06
		rrmm	0.28	0.11
		mmrr		0.11
3	42.7–43.1	rmrr	0.27	0.18
		mrrm		0.06
4	43.1–43.4	mrrr	0.35	0.18
		rrrr		0.16

[a] According to Bernoullian statistics ($P_m = 0.37, P_r = 0.63$)

Table 4 Assignment of the ^{13}C n.m.r. resonance signals of the amide carbonyl group for pentad sequences of poly(4-AHA) chains

Peak number[a]	Integration limits in ^{13}C n.m.r. δ, ppm	Sequence	Molar ratio Experimental	Molar ratio Calculated[b]
1	172.6–172.9	mm	0.15	0.14
2	172.9–173.2	rmrr		0.18
		mrmr	0.38	0.11
		mmrr		0.11
3	173.2–173.6	mmrm	0.47	0.06
		rr		0.40

[a] In the spectra, presented in *Figure 6b*

[b] According to Bernoullian statistics ($P_m = 0.37, P_r = 0.63$)

The assignment of the signals in the spectrum presented in *Figure 5* was made (*Table 3*) by analogy with that of the spectrum of the methine carbon region of poly(N,N-dimethyl-acrylamide) (PDMAA), recorded in DMSO-d_6[40]. It was taken into account that the shift of the CH* signals from high to low field reflects the inversion of the chirality of the α-carbon (four bonds removed from the observed carbon) leading to the substitution of m-unit on the end of the triad for r-unit. Such analogy of two monosubstituted polyacrylates does not seem to be contradicted since the replacement of $N(CH_3)_2$-group by $NHC_6H_3(COOH)(OH)$-group cannot be expected to result in a considerable change in the order of P_t and P_g values in different pentads as well as in considerable change in the magnitudes of γ-effect shielding[16,35]. Good agreement between experimental signal intensities and calculated pentad population (assuming Bernoullian trial) (*Table 3*) provides the support for the assumed assignment.

Amide carbonyl region. In the 125.7 MHz ^{13}C n.m.r. spectrum of poly(4-AHA) recorded in DMSO-d_6 the amide carbonyl signal proved to be insensitive to the polymer stereoregularity (*Figure 6a*), while in the spectrum recorded in D_2O amide carbonyl signal is observed in an interval of $\Delta\delta = 0.25$ ppm (173.04–173.29 ppm) and splits into three peaks due to triad and pentad sequences (*Figure 6b*).

The observed splitting can arise from two factors: the γ-*gauche* shielding effect[34] (the amide carbonyl carbon of the central unit of pentads C(O)* is affected both by shielding interactions with γ-substituent $CHC(O)NHC_6H_3(COOH)(OH)$ with probability P_t and long-range interactions[34]) and the influence of the side chain groups neighbouring to the C(O)*. However, the carbons experiencing γ-*gauche* effect are known to be only marginally influenced by the neighbours along the chain because the contribution of the γ-*gauche* effect proves to be overriding[33]. The support for such a conclusion is provided by the spectrum of the polymethacrylate poly(4-Me-AHA) recorded in DMSO-d_6 (*Figure 6c*). In spite of the fact that in the polymer chain of this sterically crowded polymer the influence of side groups is reduced considerably (due to the expansion of the backbone valence angle $C-CH_2-C$ some 15° from the normal tetrahedral value[35]) amide carbonyl signal appears to be affected by the polymer stereoregularity (*Figure 6c*). Keeping this in mind we can assume that the dependence of the C(O)* sensitivity to stereosequences upon the solvent nature (*Figures 6a* and *b*) would rather result from the solvent-induced conformation changes[41] when different bond rotations are involved in the γ-*gauche* effect in D_2O and DMSO-d_6. The solvent effect not related to the conformation (when for example, side-chain groups prove to be 'tightened' to the C(O)* due to the H-bond formation in D_2O) can be excluded from the consideration due to the assumption mentioned above.

The assignment of the amide carbonyl signals in the spectrum presented in *Figure 6b* was made (*Table 4*) on the basis of the following criteria:

(a) The assignment of triad signals of the backbone CH-group in the spectra of PDMAA[40] and poly(4-AHA) (*Figure 5*), bearing in mind the order of their increasing chemical shifts ($\delta_{mm} < \delta_{mr} < \delta_{rr}$), usually coincides with that of the increasing chemical shift of the C(O)*-signal in the central triad units of pentads[34];

(b) ^{13}C n.m.r. spectrum of the dimer bis-N,N-dimethyl-2,4-dimethylglutarylamide (DMGA) according to which amide carbonyl carbons in the *meso*-isomer resonate at higher magnetic field than r-isomer[40] taking into account that chemical shifts of the amide carbonyl carbons of both DMGA[40] and poly(4-AHA) are influenced mainly by γ-*gauche* effect;

(c) The assignment of pentad signals of carbonyl groups in the spectrum of polycyclohexylacrylate[34] when the shift of the C(O)* signal from high to low field reflects the inversion of the chirality of the α-carbon five bonds apart from the observed carbonyl and results in the substitution of an r unit on the end of triad sequence for an m unit;

(d) A comparison of the experimental signal intensities with calculated triad and pentad population assuming Bernoullian statistics.

Poly(5-AHA) spectra

Aromatic carbon region. The 125.7 MHz ^{13}C n.m.r. spectrum of poly(5-AHA) in DMSO-d_6 solution is presented in *Figure 7*. The assignment of aromatic carbon signals is carried out using additive scheme calculations[31] and DEPT sequence[32].

It is noteworthy that in this spectrum (unlike the spectrum of poly(4-AHA) presented in *Figure 1*) all aromatic carbons appear to be affected by the polymer stereoregularity. It is noticeable that in the spectrum of the sterically crowded polymethacrylate (poly(5-Me-AHA) (in which side-chain groups are remote from each other in order to reduce the repulsive interaction

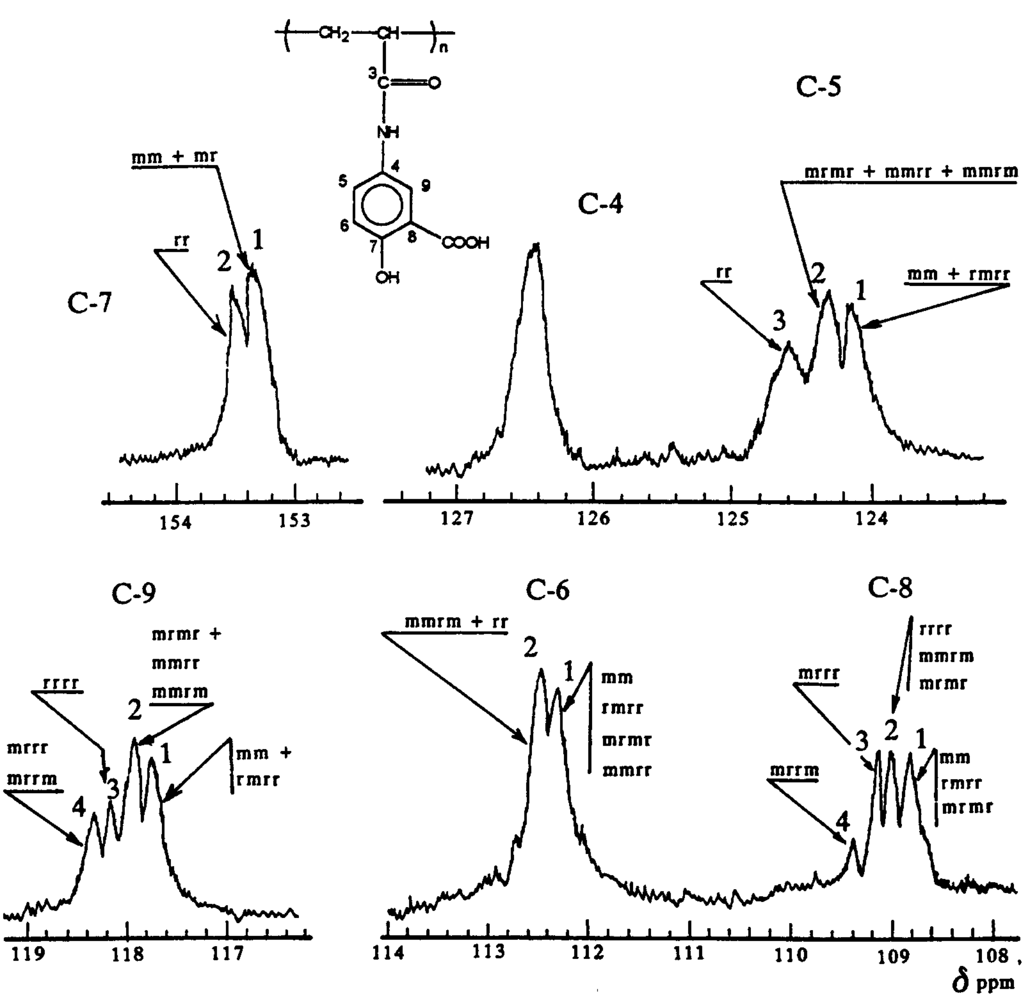

Figure 7 ^{13}C n.m.r. spectrum (125.7 MHz) of poly(5-AHA) (the aromatic carbon region) recorded in DMSO-d_6 at 70°C

between them[29]) all aromatic carbons appear to be insensitive to stereosequences. The results of calculations showed that the aromatic ring (as in the case of poly(4-AHA)) is also characterized by the lack of π-bond electron density (1.04) whereas carboxylic oxygen is characterized by the excess of π-bond electron density (0.12). Taking this into account we suggest tentatively that C^*_{arom} are influenced only by the shielding effect of the carboxylic oxygens of COOH-groups linked to the neighbouring phenyl rings but unlike poly(4-AHA) practically all aromatic carbons can approach (to more or less extent) to its shielding zone (*Figure 8*). This suggestion seems to be consistent with the data collected in *Table 5*. The order of the decreasing carbon electron density **C-8** > **C-6** > **C-9** > **C-5** > **C-4** > **C-7** does not correlate with the order of the increasing carbon sensitivity **C-4** < **C-6** < **C-7** < **C-5** < **C-9** < **C-8**. This trend can be rationalized in terms of the spatial factor D taking into consideration the data of *Table 1* according to which carbons having the value of $D \leq 5$ Å are influenced by the shielding effect of the neighbouring carboxylic oxygens. Actually, the sensitivity of the carbons having the value of $D \leq 5$ Å (**C-5**, **C-7**, **C-8** and **C-9**) appear to be more than that of carbons having the value of $D \geq 5$ Å (**C-4** and **C-6**). Keeping in mind the special geometric requirements when carbon atoms are closed to the source of shielding but on the periphery of the shielding zone[36,37], we can suggest tentatively that carbons **C-5**, **C-8** and **C-9** would rather extend into the shielding zone of the neighbouring carboxylic oxygens whereas carbons **C-4**, **C-6** and **C-7** appear to be on the periphery of this zone (*Figure 8*).

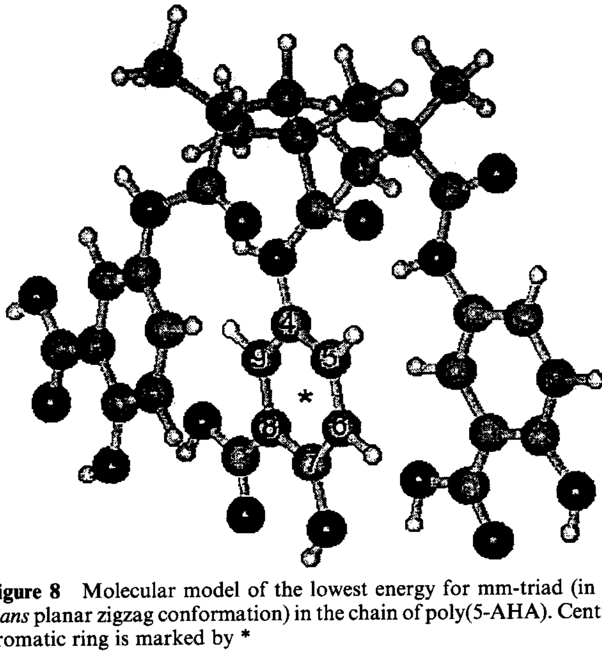

Figure 8 Molecular model of the lowest energy for mm-triad (in all *trans* planar zigzag conformation) in the chain of poly(5-AHA). Central aromatic ring is marked by *

Table 5 Assignment of the ^{13}C n.m.r. resonance signals of the aromatic carbons for triad and pentad sequences of poly(5-AHA) chains and the comparative analysis of their sensitivity to stereo-sequences

Aromatic carbon	Peak number	Integration limits in ^{13}C n.m.r. δ, ppm	Sequence	Molar ratio	
				Experimental	Calculated[a]
C-8	1		mm		0.16
(4.19)[b]		108.5–108.9	rmrr	0.42	0.17
[4.70][c]			mmrr		0.11
	2		mrmr		0.11
		108.9–109.1	mmrm	0.30	0.08
			rrrr		0.13
	3	109.1–109.3	mrrr	0.20	0.17
	4	109.3–109.5	mrrm	0.08	0.06
C-6	1		mm		0.16
(4.16)		112.0–112.4	rmrr	0.55	0.17
[5.50]			mrmr		0.11
			mmrr		0.11
	2	112.4–112.8	mmrm	0.45	0.08
			rr		0.36
C-5	1	123.9–124.2	mm	0.34	0.16
(4.08)			rmrr		0.17
[5.15]	2	124.2–124.4	mrmr		0.11
			mmrr	0.29	0.11
			mmrm		0.08
	3	124.4–124.9	rr	0.36	0.36
C-9	1	117.5–117.8	mm	0.34	0.16
(4.10)			rmrr		0.17
[5.11]	2	117.8–118.1	mrmr		0.11
			mmrr	0.30	0.11
			mmrm		0.08
	3	118.1–118.3	rrr	0.16	0.13
	4	118.3–118.5	mrrr	0.20	0.17
			mrrm		0.06
C-7	1	153.0–153.4	mm	0.65	0.16
(3.86)			mr		0.48
[4.86]					
	2	153.4–153.7	rr	0.35	0.36
C-4	1	126.5			
(3.97)					
[5.78]					

[a] According to Bernoullian statistics ($P_m = 0.32$, $P_r = 0.68$)

[b] Mulliken electron densities calculated by MOPAC version 6.0[22]

[c] The average space distance between C^*_{arom} and carboxylic oxygens of the first neighbouring phenyl rings, Å, measured in the molecular model of the mm-triad in the poly(5-AHA) chain (*Figure 9*) by the computer program Hyperchem version 4.5[26]

In the spectrum presented in *Figure 7* signals of aromatic carbons **C-5**, **C-7**, **C-8** and **C-9** can provide the information upon the microstructure of the poly(5-AHA) chains at the triad and pentad level. Signals **C-8** and **C-9** are observed in intervals of $\Delta\delta = 0.73$ ppm (108.67–109.40 ppm) and $\Delta\delta = 0.59$ ppm (117.79–118.37 ppm), respectively, and split into four peaks; signal **C-5** is observed in an interval of $\Delta\delta = 0.43$ ppm (124.17–124.60 ppm) and split into three peaks; signals **C-7** and **C-6** are observed in intervals of $\Delta\delta = 0.19$ ppm (153.32–153.51 ppm) and $\Delta\delta = 0.08$ ppm (112.38–112.46 ppm), respectively, and split into two peaks.

Low field component of the **C-8** carbon signal (peak 4, *Figure 7*) was assumed to correspond to **mrrm** pentad, taking into account that in this pentad substituents the side substituents responsible for the shielding effect ($\mathbf{R}^{\alpha}$ and $\mathbf{R}_1^{\beta}$) are remote from $\mathbf{R}^*$. The Bernoullian probabilities P_m and P_r (being 0.32 and 0.68, respectively) were obtained from the experimental estimate (using relative intensity of peak 4) of the **mrrm** pentad content. The complete signal assignment (*Table 5*) was made using the same criteria applied to the assignment in the poly(4-AHA) spectrum. It is noteworthy that chemical shifts of the C^*_{arom} in mm-triad prove to be insensitive to the stereochemical configuration of the monomeric unit on each end of this sequence (i.e. to pentad structure). This

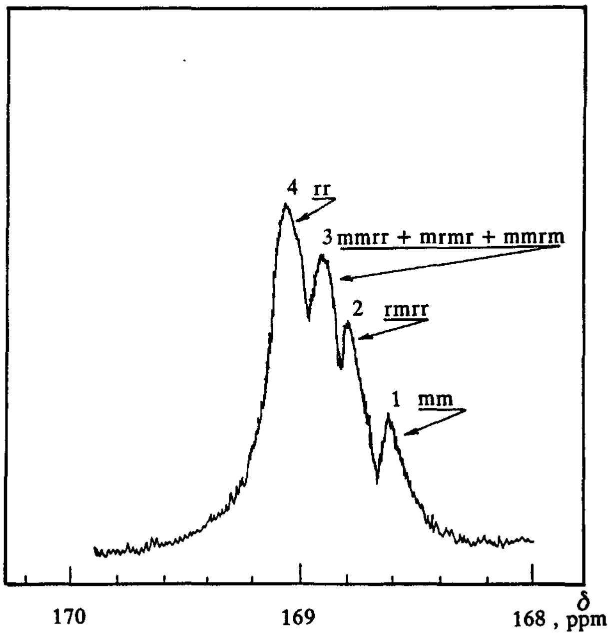

Figure 9 125.7 MHz ^{13}C n.m.r. spectrum of poly(5-AHA) (the amide carbonyl region) recorded in DMSO-d_6 at 70°C

observation reflects the fact that deshielding effect produced by R_2^{β} appears to be weak. Such weakness may be tentatively attributed to such conformation prevalent in mm-centred pentads (which can be assumed to be more sterically constrained than mr- and rr-centred ones) when bulky neighbouring side-chain substituents are remote from each other (*Figure 8*) and their influence on the C^*_{arom} is reduced.

Amide carbonyl region. In the 125.7 MHz ^{13}C n.m.r. spectrum of poly(5-AHA) recorded in DMSO-d_6 (*Figure 9*) the amide carbonyl signal appeared to be considerably affected by the polymer stereoregularity unlike the analogous signal in the spectrum of poly(4-AHA) obtained under the same conditions (*Figure 6a*). Assuming that the sensitivity of the amide carbonyl signal to stereosequences arises mainly from the γ-*gauche* effect (with conformation probability P_t[40]), we can explain this observation in terms of conformational changes. Actually, a comparison of molecular models of the lowest energy for mm-triads presented in *Figures 3* and *8* clearly shows that side substituents $C(O)NHC_6H_3(COOH)(OH)$ in the polymer chain of poly(5-AHA) are more expanded from each other (*Figure 8*) than in the polymer chain of poly(4-AHA) (*Figure 3*). This trend can probably reflect the fact that poly(5-AHA) can be considered a more sterically crowded polymer having bulkier side substituent than poly(4-AHA) because of the different relative spatial position of the bulky COOH groups attached to the neighbouring aromatic rings (*Figures 3* and *8*). Increasing the size of substituents is known[39] to result in a less fractional contribution of TTTT-conformation in rr-triad and TTTG-conformation in mr-triad. Hence, in poly(5-AHA) chain (in comparison with poly(4-AHA)) values of P_t (and as a consequence γ-*gauche* shielding effect) would decrease both for mr- and rr-triads in comparison with the mm-triad, which probably leads to the chemical shift dispersion among the various stereosequences observed in the spectrum of poly(5-AHA).

The assignment of the amide carbonyl signals in the spectrum presented in *Figure 9* was made (*Table 6*) using the same criteria applied to the amide carbonyl signal assignment in the spectrum of poly(4-AHA) recorded in D_2O (*Figure 6b*).

CONCLUSIONS

The stereochemical structure of poly(4-AHA) and poly(5-AHA) was analysed by ^{13}C n.m.r. spectroscopy. It was assumed that the chemical shift dispersion among the various sequences observed for aromatic carbon signals arises mainly from the influence of the neighbouring side-chain substituents, while stereosequence dependent chemical shifts of amide carbonyl signal result from the γ-*gauche* effect. For poly(4-AHA) it was suggested that in the spectrum recorded in D_2O aromatic carbon signals were influenced mainly by the ring current from the neighbouring phenyl rings, whereas those in the spectrum recorded in DMSO-d_6 were influenced by the shielding effect of the carboxylic oxygens of COOH-groups linked to the neighbouring phenyl rings. This solvent-induced effect was explained in terms of H-bonds, which seem to block the carboxylic oxygens and to 'tighten' phenyl rings to each other. For poly(5-AHA) it was assumed that aromatic carbon signals in the spectrum recorded in DMSO-d_6 were influenced both by the shielding effect of carboxylic oxygens and ring current of phenyl rings. These assumptions are consistent with the total electronic charge of the π-aromatic bonds in poly(4-AHA) and in poly(5-AHA) and with that of carboxylic oxygens. The sensitivity of aromatic carbon signal to stereosequences was found to depend mainly upon the spatial vicinity of the carbon to maximum of the shielding zones of phenyl rings and carboxylic

Table 6 Assignment of the ^{13}C n.m.r. resonance signals of the amide carbonyl group for pentad sequences of poly(5-AHA) chains

			Molar ratio	
Peak number	Integration limits in ^{13}C n.m.r. δ, ppm	Sequence	Experimental	Calculated[a]
1	168.5–168.7	mm	0.15	0.16
2	168.7–168.8	rmrr	0.19	0.17
3	168.8–169.0	mmrr		0.11
		mrmr	0.28	0.11
		mmrr		0.08
4	169.0–169.3	rr	0.38	0.36

[a] According to Bernoullian statistics ($P_m = 0.32$, $P_r = 0.68$)

oxygens. For poly(4-AHA) it was observed that in the spectrum recorded in D_2O (unlike the spectrum recorded in DMSO-d_6) the amide carbonyl proved to be affected by the polymer stereoregularity. This trend was rationalized in terms of the solvent-induced conformational changes. It was found that in the spectrum of poly(5-AHA) recorded in DMSO-d_6 (unlike the analogous spectrum of poly(4-AHA)) the amide carbonyl signal proved to be sensitive to the polymer chain microstructure. This observation was assumed to reflect the conformation changes induced by the transfer from poly(4-AHA) polymer to more sterically crowded poly(5-AHA) having bulkier side substituent. The microstructural analysis of both poly(4-AHA) and poly(5-AHA) chains which was carried out at triad and pentad level showed that the chain propagation of both polyacrylates prepared by radical polymerization could be ascribed to Bernoullian statistics.

ACKNOWLEDGEMENTS

The authors thank the DGCYT for financial support (grant MAT96-0981) and supporting A.B. during her sabbatical year.

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