Stereochemical Structure of Poly(cyclohexyl acrylate) Studied by One-Dimensional and Two-Dimensional $^{13}C-^{1}H$ Spectroscopy

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ABSTRACT: The stereochemical structure of poly(cyclohexyl acrylate) (PCHA) prepared under different polymerization conditions was studied by the combination of one- and two-dimensional ^{13}C NMR methods. The assignments of the triad, tetrad, and pentad signals were carried out according to conformational and configurational approaches. In general, the sensitivity of the observed ^{13}C NMR signals assigned to sequences of triad and tetrad is well reproduced by the ^{13}C chemical shifts estimated via the γ-gauche effect method. For PCHA prepared by radical and anionic polymerization (using different solvents and catalysts), a first-order Markov model is required to fit the observed intensities at the tetrad and pentad level, rather than the classical Bernoullian statistics.

Introduction

Homo- and copolyacrylates are of great interest in many industrial applications, e.g., as coating systems, optical materials, membranes, and adhesive sealants, and also are of medical interest due to their properties as supports for compounds with pharmacological activity. Such a wide range of applications arises from the wide range of physical and chemical properties that can be covered by an appropriate choice of side groups and copolymer systems. For example, PCHA, which is the subject of the present investigation, is characterized by good thermal properties and high flexibility at relatively low temperature.

The physical and chemical properties proved to be influenced fundamentally by the microstructure of these polymers, which involves the character of the monomer distribution in the polymer chain and stereochemical arrangement of various groups (tacticity). Thus, the determination of configuration sequence distribution appears to be important.

NMR spectroscopy has been found to be the most efficient technique for characterizing the stereochemical structure of polymers, because chemical shift is sensitive to the configurational structure in sequences of monomer units.[1,2] Polyacrylates have been the subject of many ^{1}H NMR studies[3−6] which have made major contributions to the understanding of the stereochemical configuration of synthetic macromolecules. Since 1970, one-dimensional (1D) ^{13}C NMR spectroscopy has become the method of choice for investigating the polyacrylate microstructure[7−10] due to its large chemical shift range, which results in greater sensitivity to structural detail. Recently, the microstructure of polyacrylates was studied by the application of the HMQC (heteronuclear multiple-quantum correlation) two-dimensional (2D) $^{1}H-^{13}C$ NMR method,[11,12] but the stereochemistry of PCHA has not been studied before. The goal of the work described in this paper was to investigate the stereochemical structure of PCHA by means of the combination of one- and two-dimensional ^{13}C NMR methods and also to estimate the possibility of application of the γ-gauche effect method to the analysis of stereosequence-dependent chemical shifts in the carbon spectra of PCHA.

Experimental Section

Model Compounds. Dicyclohexyl 2,4-dimethylglutarate (DCHDMG) was prepared by direct condensation of 2,4-dimethylglutaric acid with cyclohexanol in a solution of dry toluene as described elsewhere.[13]

Cyclohexyl acrylate was prepared by the reaction of cyclohexanol with acryloyl chloride in a solution of NaOH at 0 °C.

Polymers. Poly(cyclohexyl acrylates) (PCHA). PCHAI. Cyclohexyl acrylate was polymerized in toluene at −82 °C for 3 h using phenylmagnesium bromide (PhMgBr) as catalyst for anionic polymerization. The number-average molecular weight M_n measured by GPC was found to be 25 000 with a polydispersity index (PI) $M_w/M_n = 1.08$.

PCHAII. Cyclohexyl acrylate was polymerized in tetrahydrofuran (THF) at −82 °C for 3 h using *n*-butyllithium (*n*BuLi) as catalyst for anionic polymerization. The value of M_n determined by GPC was 36 000 with PI = 1.15.

PCHAIII. Cyclohexyl acrylate was polyymerized in toluene at −82 °C for 3 h with *n*BuLi as catalyst for anionic polymerization. The value of M_n determined by GPC was 42 000 with PI = 1.21.

PCHAIV. Cyclohexyl acrylate was polymerized in toluene at 50 °C for 6 h by free radical polymerization using 2,2′-azobis(isobutyronitrile (AIBN) as described previously.[14] The value of M_n determined by GPC was 150 000 with PI = 1.86.

NMR Measurements. One-dimensional ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer (operating at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR) at 50 °C using 15% (w/v) solutions in $CDCl_3$ with hexamethyldisiloxane (HMDS) as an internal reference. All chemical shifts cited are referred to HMDS. All spectra were recorded via Fourier transformation of time-domain data.

Two-dimensional spectra of PCHAI and PCHAIV were recorded on a Varian Unity-500 spectrometer (operating at 499 MHz for ^{1}H NMR and 125.7 MHz for ^{13}C NMR) at 50 °C using

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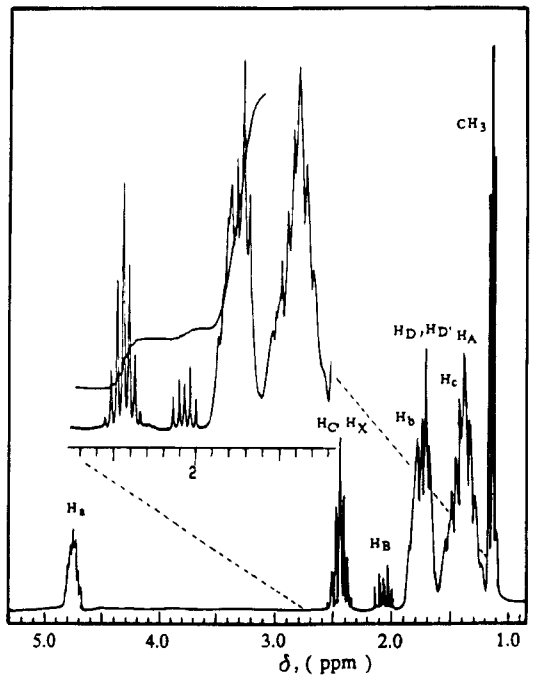


Figure 1. ^{1}H NMR spectrum of the model compound dicyclohexyl-2,4-dimethylglutarate (DCHDMG).

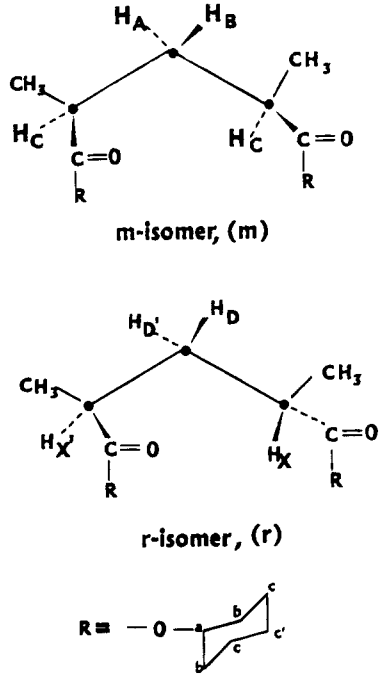
10% (w/v) solutions in $CDCl_3$. Sequence HMQC (heteronuclear multiple-quantum correlation),[15,16] which enables us to achieve a much higher sensitivity compared to classical HETCOR, was applied. A total of 16 scans were accumulated over 512 t_1 increments with a relaxation delay of 0.9 s. Frequency ranges of 1040 and 2900 Hz were used in the carbon and proton dimensions, respectively. A sine-bell apodization function with a phase shift was applied in both dimensions prior to Fourier transformation. The total acquisition time was 4–6 h for every experiment.

Results and Discussion

Analysis of Diad Sequences. Usually, the conformation population of diad sequences in polymer chains is studied on the basis of model compounds.[17–19] In Figure 1 proton NMR spectrum of DCHDMG (modeling the diad sequences in the polymer chain of PCHA) is shown. The assignments of signals (see Figure 1 and Scheme 1) clearly show that using this proton spectrum, one can determine the following J couplings: J_{BC} in the m isomer analyzing the splitting of peak H_B, which is a doublet of triplets J_{BC} = 6.6 Hz and J_{AB} = 13 Hz; J_{CMe} (in the m isomer) and J_{XMe} (in the r isomer) analyzing the splitting of the Me signal, which is the superposition of two doublets with 6.6 Hz peak separations. Thus, $J_{CB} = J_{CMe} = J_{XMe}$ = 6.6 Hz. The determination of J_{AC} in the m isomer and J_{DX} and $J_{D'X}$ in the r isomer is not possible due to the overlapping of the signals of the cyclohexyl ring protons (b,c) with those of H_A, H_D, $H_{D'}$. Nevertheless, some information on the values of J_{AC}, J_{DX}, and $J_{D'X}$ can be obtained from the analysis of the multiplicity of the signals corresponding to the H_C and H_X protons in the m and r isomers, respectively (Figure 1). The signals H_X are the superposition of quartets (J_{XMe} = 6.6 Hz) and doublets ($J_{XD} = J_{XD'}$ = 6.6 Hz). If $J_{XD} \neq J_{XD'}$ the signals H_X would give a more complex multiplet.[17–19] The signal H_C is the superposition of a quartet (J_{CMe} = 6.6Hz) and two doublets ($J_{CA} = J_{CB}$ = 6.6 Hz). If $J_{CA} \neq J_{CB}$, the signal H_C would give a more complex multiplet.[17–19]

These observations show that $J_{XD} = J_{XD'} = J_{CA} = J_{CB}$ = 6.6 Hz. By means of the J couplings obtained, we

Scheme 1. Structural Formulas of m and r Isomers of DCHDMG in Terms of Planar Zigzag Conformation



determined using Bovey's method[17–19] that the most stable conformation for the r isomer of the model compound (and hence for the r diad in the PCHA chain) should be the GG conformation. This conclusion correlates with the conformational preference of 2,4-disubstituted pentanes and 2,4,6-trisubstituted heptanes:[20] increasing substituent size (Cl < Ph < $C(O)OCH_3$ < $C(O)OC_6H_{11}$) results in a greater fractional contribution of the GG conformation in the r diad, the GGTT conformation in the rr triad, and the GGTG conformation in the mr triad.

Using the relative intensities of signals H_X, H_C, and H_B, we also calculated the isomer composition of the dimer as m = 56% and r = 44%. On this basis one can assign the signals of the m (more intense ones) and r isomers in the carbon spectrum of the model compound (Figure 2).

Keeping in mind that DCHDMG reproduces the diad sequence in the polymer chain of PCHA, we can assume that the main-chain CH_2 group in the m diad appears to be more shielded than in the r diad.

Analysis of Triad Sequences. In the carbon spectra of PCHA, one can observe the splitting of the main-chain CH group into two (Figure 3A) and three (Figure 3B–D) peaks due to triad sequences. Polyacrylates prepared by anionic polymerization at low temperature with PhMgBr as catalyst are known to be predominantly isotactic.[21] Therefore comparison of the spectra shown in Figure 3B–D with the spectrum in Figure 3A enables us to assign the upper field peak (at 40.75 ppm) to the mm triad, which is consistent with the assignment of the m and r signals for the CH groups of DCHDMG.

The two-dimensional HMQC NMR spectrum of the predominantly isotactic PCHA is presented in Figure 4. If we assume that the signal of the CH group at 40.75 ppm corresponds to the mm triad, the most intense peak of the CH_2 group should be ascribed to the mmm tetrad because the populations of the other tetrads (as shown by calculations[1]) are negligible. Actually, since the mmm tetrad contains magnetically nonequivalent meth-

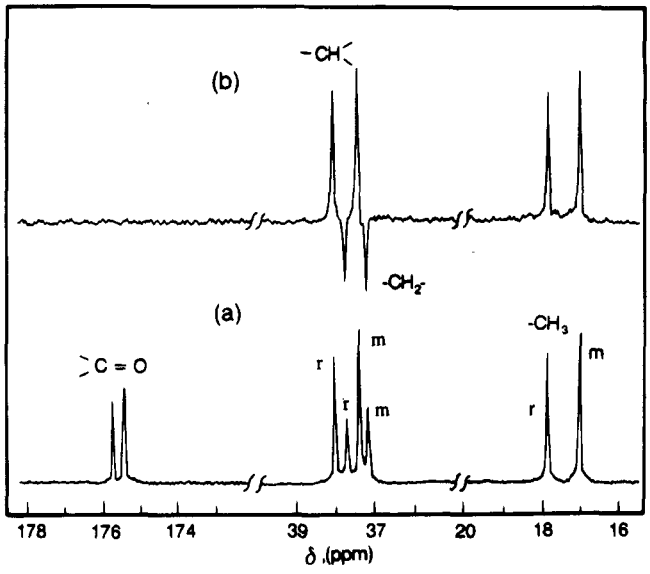


Figure 2. ^{13}C NMR spectra of the model compound DCH-DMG: decoupled spectrum (a); spectrum recorded using DEPT sequence (b).

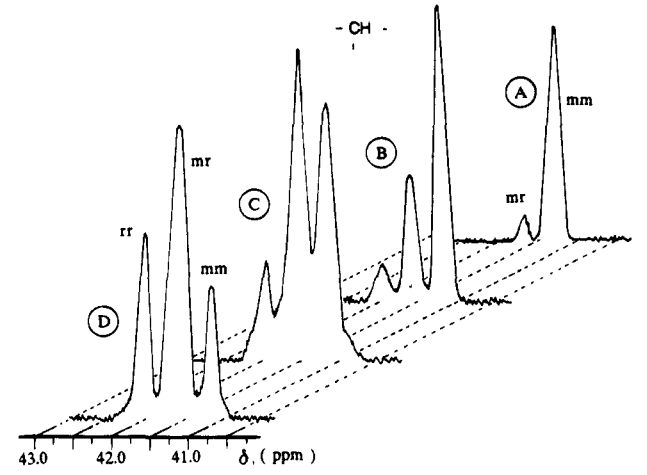


Figure 3. Carbon spectra (region of the main-chain CH group signals) of PCHAI (A), PCHAII (B), PCHAIII (C), and PCHAIV (D).

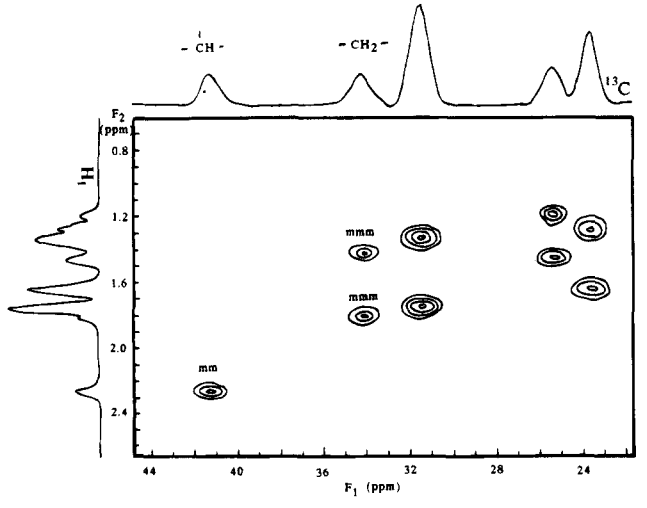


Figure 4. Two-dimensional ($^{13}C-^{1}H$) HMQC NMR spectrum of a 10% solution of PCHAI in $CDCl_3$ recorded at 50 °C.

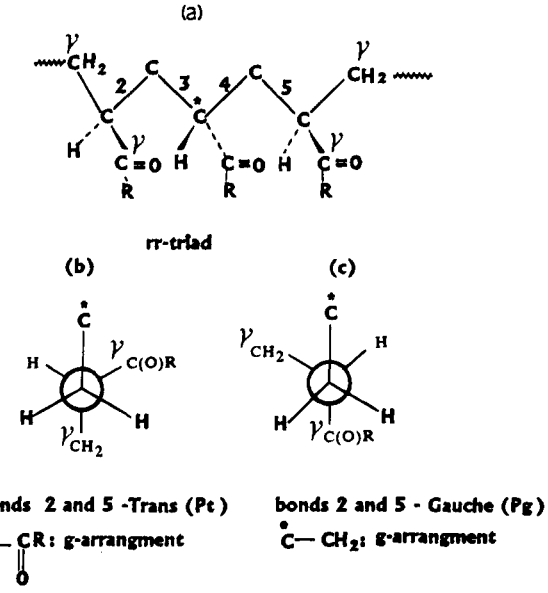
ylene protons, the appearance of two correlation peaks for the respective carbon (CH_2) in the HMQC spectrum argues in favor of the suggested assignment (Figure 3).

Table 1. Assignment of the ^{13}C NMR Resonance Signals of the Main-Chain CH Group for the Triad Sequences of the PCHA Chains: Application of the γ-Gauche Effect Method

chem shift δ, ppm	triad	bond conformation probability P_t	bond conformation probability P_g	total shielding effect,[a] ppm
40.75	mm	0.40	0.60	−5.4
41.15	mr	0.59	0.41	−5.6
41.65	rr	0.69	0.31	−5.7

[a] $\gamma_{CH-C(O)OR} = -6.0$ ppm; $\gamma_{CH-CH_2} = -5.0$ ppm are assumed to be applicable.

Scheme 2. (a) rr Triad in All-Trans Planar Zigzag Conformation and (b,c) Newman Projections along bonds 2 and 5 of rr Triad



The assignment of the triad signals (see Figure 3 and Table 1) can also be interpreted in light of the correlation between the ^{13}C NMR chemical shifts and the triad conformation.[22-26] According to Tonelli[22] the central CH group of the triads is experiencing γ-gauche shielding effects, produced by the γ-substituent C(O)OR ($\gamma_{CH-C(O)OR}$) with a conformation bond probability P_t and by the γ-substituent CH_2 (γ_{CH-CH_2}) with a conformation bond probability P_g (see Scheme 2). The value of $\gamma_{C-C(O)OR}$, determined by the procedure illustrated in Scheme 3, seems to be higher than γ_{C-CH_2} because the value of P_g for cyclohexyl butyrate is considered to be lower than for butane due to more severe steric hindrance of the bulkier γ-substituent $C(O)OC_6H_{11}$ with the C^*H_3 group. Values of P_t and P_g for different triads were calculated on the basis of data for the conformation preferences for 2,4,6,-trisubstituted heptane in modeling the triad sequences in the polymer chain of poly(methyl acrylate) (PMA).[20] The results of the application of the γ-gauche effect method for prediction of the relative chemical shifts of the triad signals are presented in Table 1. The data of this table clearly show good agreement between the estimated (all triads have a similar shielding effect) and the observed chemical shifts for the CH signals of PMA, which are little affected by the stereoregularity of the polymer.[7] Increasing substituent size ($C(O)OC_6H_{11}$ seems to be bulkier than $C(O)OCH_3$) is known[1] to result in a greater fractional contribution of the GGTT conformation in the rr triads and the GGTG conformation in the mr triads. Hence, in PCHA chains (in comparison with PMA) values of P_g would increase (and consequently P_t would decrease) for both the mr

Scheme 3. Determination of the γ-Gauche Shielding Effect Produced by γ-Substituents C and C(O)OR (R = Cyclohexyl) (See Text) and Newman Projections along Bond 2

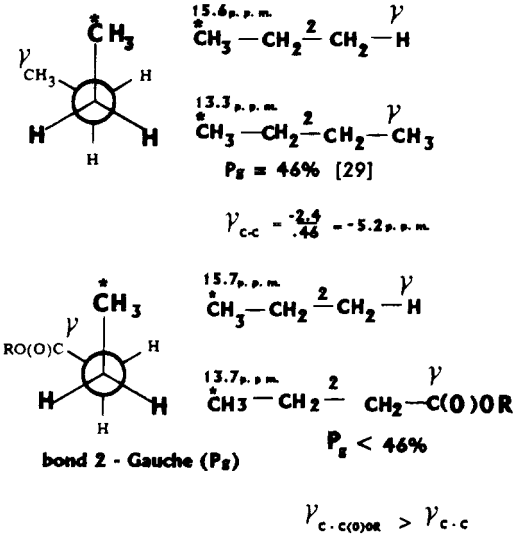


Table 2. Comparative Stereochemical Parameters of PCHA Obtained under Different Polymerization Conditions

PCHA	polymerization conditions	triad molar fraction mm	mr	rr	$P_{m/r} + P_{r/m}$
I	anionic, PhMgBr, toluene, −82 °C	0.93	0.07	0.0	1.04
II	anionic, *n*BuLi, THF, −82 °C	0.62	0.29	0.09	0.81
III	anionic, *n*BuLi, toluene, −82 °C	0.40	0.41	0.19	0.88
IV	radical, AIBN, toluene, +50 °C	0.23	0.46	0.31	0.93

and the rr triads. Keeping in mind that $\gamma_{CH-CH_2} < \gamma_{CH-C(O)OR}$, we can predict the decrease of the total shielding effect for both the mr and the rr triads in comparison with the mm triad. Thus in the methine region of PCHA (also as for PMA) the correspondence between the observed chemical shifts and those estimated via the γ-gauche effect method is close.

From the ratio of the triad peak areas, one can determine important characteristics describing the polymer chain such as the triad molar fraction and the conditional probabilities ($P_{m/r}$, $P_{r/m}$).[1] The data collected in Table 2 show clearly that deviation from Bernoullian statistics increases in the order PCHAI < PCHAIV < PCHAIII < PCHAII. Thus, the chain propagation of PCHA prepared by anionic polymerization with *n*BuLi as catalyst cannot be described by Bernoullian statistics. The data of Table 2 also allow us to draw the following conclusion: for PCHA prepared by anionic polymerization at −82 °C, the isotacticity extent (IE) increases in the order toluene < THF, *n*BuLi < PhMgBr. Noteworthy for PMA, the value of IE increases in the opposite order: PhMgBr < *n*BuLi.[3]

Analysis of Tetrad Sequences. The main-chain CH_2 signals appear in an interval of $\Delta\delta \simeq 4.5$ ppm (33.5−38.0 ppm) and split into five peaks due to tetrad sequences (Figure 5B−D). In the carbon spectrum of predominantly isotactic PCHA, only two peaks (Figure 5A) are observed. It is noteworthy that in this spectrum the most intense peak, corresponding to the mmm tetrad, appears to be unsymmetrical, probably because of slightly different chemical shifts reflecting the hexad structure: mmmmm (calculated population 82%) and mmmmr (calculated population 7%). Thus, the mmm tetrad in PCHA (as in the poly(vinyl chloride) (PVC) chain[24]) proved to be sensitive to the stereochemical configuration of the monomeric unit on each end of this sequence being compressed due to its preferred helix.[24]

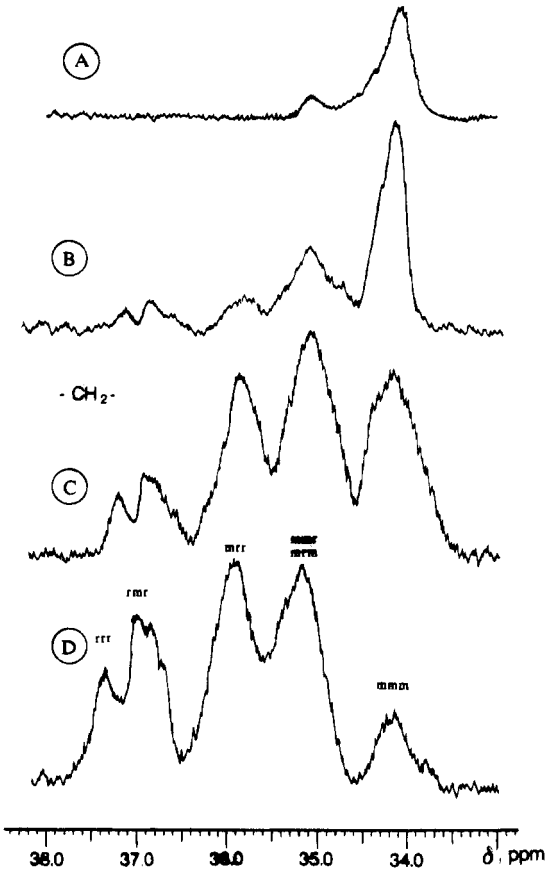


Figure 5. Carbon spectra (region of the main-chain CH_2 group signals) of PCHAI (A), PCHAII (B), PCHAIII (C), and PCHAIV (D).

Table 3. Assignment of the ^{13}C NMR Resonance Signals of the Main-Chain CH_2 Group for the Tetrad Sequences of the PCHA Chains

integration limits in ^{13}C NMR δ, ppm	tetrad	tetrad molar ratio PCHAII exp	PCHAII calc[a]	PCHAIII exp	PCHAIII calc[a]	PCHAIV exp	PCHAIV calc[a]
33.5−34.5	mmm	0.55	0.50	0.27	0.26	0.11	0.12
34.5−35.5	mrm		0.09		0.11		0.10
		0.29		0.35		0.32	
	mmr		0.24		0.27		0.23
35.5−36.5	mrr	0.08	0.11	0.19	0.19	0.26	0.26
36.5−37.0	rmr	0.05	0.03	0.09	0.07		0.12
						0.31	
37.0−38.0	rrr	0.03	0.03	0.08	0.09		0.17

[a] According to first-order Markov statistics.

The assignment of the tetrad peaks (see Figure 5 and Table 3) was made according to the following criteria: (i) comparison of the experimental signal intensities with the calculated tetrad population assuming first-order Markov statistics;[1] (ii) comparison of the intensities of various resonances in the spectrum of the predominantly isotactic PCHA (Figure 5A) with those of PCHA prepared under other polymerization conditions (Figure 5−D); (iii) by recording the two-dimensional HMQC NMR spectrum (Figure 6).

The assignment of the 2D HMQC spectra is based on the fact that, of the six NMR-resolvable tetrad sequences (mmm, mmr, rmr, mrm, mrr, and rrr), three tetrads have magnetically nonequivalent CH_2 protons (mmm, mmr, and rmr) and three have magnetically

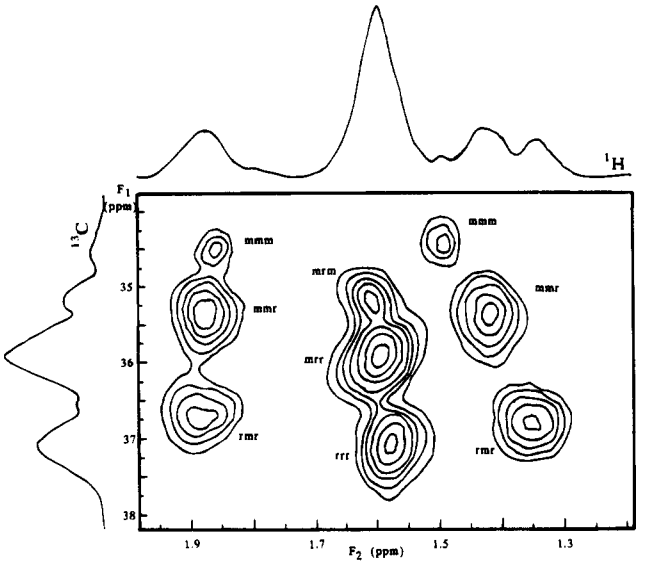


Figure 6. Two-dimensional (^{13}C–^{1}H) HMQC NMR spectrum of a 10% solution of PCHAIV in $CDCl_3$ recorded at 50 °C.

equivalent CH_2 protons (rrr, mrr, and mrm). In such a case, the 2D HMQC spectrum allows one to define the central units of the tetrad sequences: the central m unit gives two correlation peaks for the respective carbon signal; the central r unit gives one correlation peak. The existence of three correlation peaks for the respective carbon signal proves that the signal of the tetrad with the m central units overlaps the signal of the tetrad with the central r unit etc.

The 2D HMQC spectrum also enables us to identify signals of different tetrads with a central m unit (i.e., mmm, mmr, amd rmr). Analysis of 2D HETCOR spectra of polyacrylates reported by Suchoparek[11] demonstrates that the separation between two correlation peaks associated with a central m unit (i.e., chemical shift difference between two nonequivalent protons) increases in the order rmr > rmm > mmm. Moreover, the chemical shift of the anti methylene proton (see Scheme 4) increases in the opposite order: mmm > mmr > rmr. Scheme 4, illustrating the structure of tetrads with a central m unit, explains this observation: while an R^α substituent is known to produce a deshielding effect at the methylene protons of a central m unit,[3-6] an R^β substituent seems to produce a shielding effect.

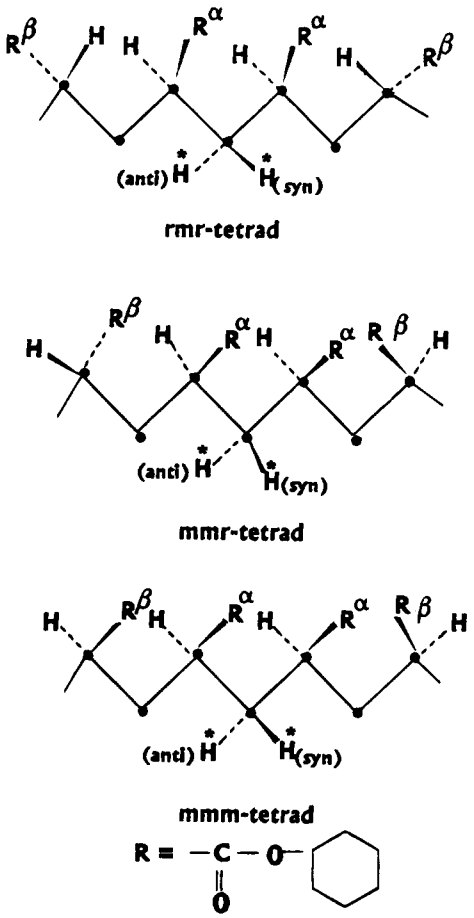
Tetrad assignments made according to the criteria mentioned above (see Figure 5 and Table 3) are consistent with the fact that in the spectrum of the dimer (Figure 2), the methylene carbon signal of the meso isomer appears at a higher field than that of the racemic one, as indicated above.

Good agreement between experimental and calculated tetrad contents for PCHAII, PCHAIII, and PCHAIV (Table 3) not only supports the assignment but also demonstrates that the propagation of PCHA chains prepared under different polymerization conditions can be better described by first-order Markov statistics than Bernoulian statistics. Values of Ω, defined by Coleman and Fox[27] as a measure of the deviation from first-order Markov statistics, decrease in the order PCHAII (1.13) > PCHAIV (1.04) > PCHAIII (1.0).

The application of the γ-gauche effect method to the analysis of the tetrad signals requires that at least two assumptions be taken into account:

(i) The central CH_2 group of tetrads (C^*H_2) is experiencing a γ-gauche shielding effect, produced by the γ-substituent CHC(O)OR ($\gamma_{CH_2-CHC(O)OR}$) with a probability P_g (g-1,4 interaction) (see Scheme 2c). When the procedure illustrated in Scheme 3 was applied to propane, $C^*H_3CH_2CH_2(H)^\gamma$, and cyclohexyl valerate, $C^*H_3CH_2CH_2(CH_2C(O)OR)^\gamma$, we found that γ_{C-C} and $\gamma_{C-CC(O)OR}$ have practically the same value due to the weak electron acceptor properties of the C(O)OR group.

Scheme 4. Structure of Tetrads with a Central m Unit in Terms of the Planar Zigzag Conformation. Observed Protons are Marked by an Asterisk



(ii) The chemical shift of the C^*H_2 group is known to be sensitive to long-range interactions.[28] Thus, the CH group attached directly to the C^*H_2 group (CH^α) is also experiencing γ-gauche shielding effects. These shielding interactions of the CH^α group probably reduce the deshielding effect it produces at the C^*H_2 group (g-1,5 interaction). Therefore, the more g-1,4 and g-1,5 interactions the C^*H_2 group is experiencing in its average conformation environment, the more shielded the carbon becomes. This conclusion would predict the order of the CH_2 tetrad stereosequence resonances as (rmr + rrr), (mmr + mrr), (mrm + mmm) from low to high field, and this order agrees qualitatively with that observed experimentally (Figure 5 and Table 3).

Analysis of Pentad Sequences. The carbonyl signals are observed in an interval of 0.7 ppm (173.1–173.8 ppm) and split into four peaks (Figure 7B–D) due to the pentad sequences. In the carbon spectrum of the predominantly isotactic PCHA, only three peaks (Figure 7A) are observed. The assignment of these peaks (Table 4) was made using the same criteria (with the exception of the 2D HMQC spectra) applied to the assignments of the tetrad sequences.

Comparison of the data presented in Table 1 (assignment of the main-chain CH group signals for the triads)

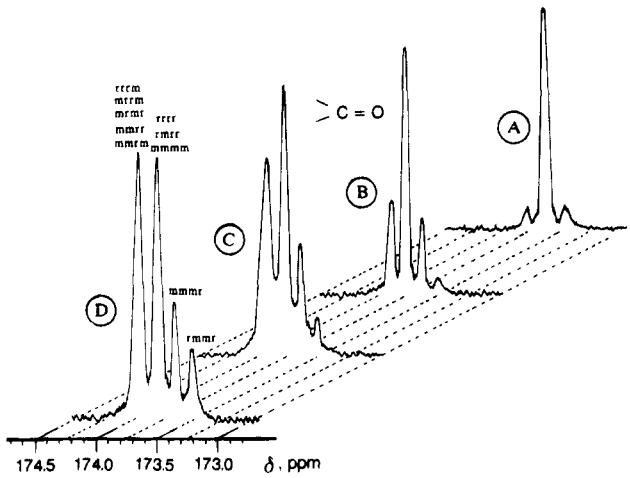


Figure 7. Carbon spectra (region of carbonyl group signals) of PCHAI (A), PCHAII(B), PCHAIII (C), and PCHAIV (D).

Table 4. Assignment of the ^{13}C NMR Resonance Signals of the Ester Carbonyl Group for the Pentad Sequences of the PCHA Chains

		pentad molar ratio					
		PCHAII		PCHAIII		PCHAIV	
integration limits in ^{13}C NMR δ, ppm	pentad	exp	calc[a]	exp	calc[a]	exp	calc[a]
173.1–173.3	rmmr	0.03	0.02	0.05	0.04	0.07	0.06
173.3–173.5	mmmr	0.19	0.19	0.19	0.18	0.13	0.12
173.5–173.6	mmmm		0.40		0.17	0.27	0.05
	rmrr	0.44	0.02	0.32	0.07		0.15
	rrrr		0.01		0.04		0.09
	mmrm		0.15		0.14		0.10
173.6–173.8	mmrr		0.09	0.44	0.13	0.53	0.14
	mrmr	0.35	0.04		0.08		0.10
	mrrm		0.03		0.05		0.05
	rrrm		0.04		0.09		0.14

[a] According to first-order Markov statistics.

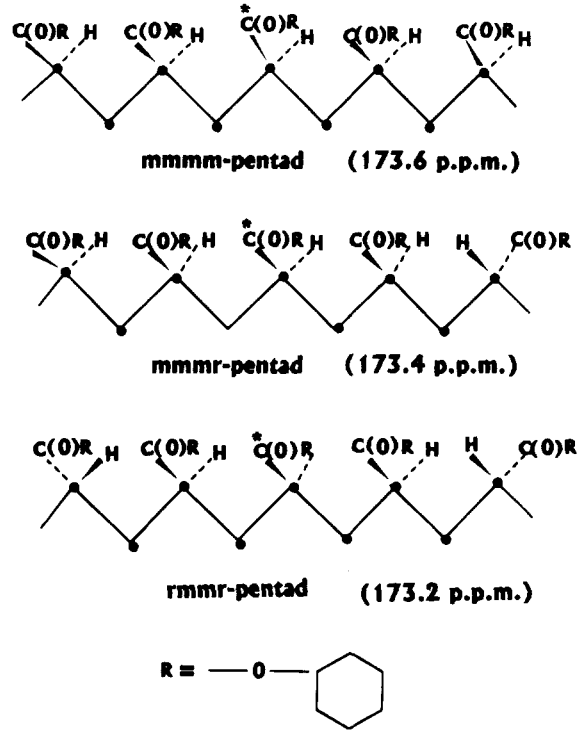
with those presented in Table 4 clearly shows that the chemical shift of the C*(O) group signals in the central triad units of the pentads increases in the same order as the chemical shift of the CH group signals in the triads (i.e., mm < mr < rr).

The application of the γ-gauche effect method to the analysis of the pentad signals requires that the following assumptions be taken into account:

(i) The central C(O) group of the pentad (C*(O)) is experiencing a γ-gauche shielding effect, produced by the γ-substituent CHC(O)OR ($\gamma_{C(O)-CHC(O)OR}$) with a probability P_t (g-1,4 interaction) (Scheme 2b). The C(O)OR substituents six bonds apart from C*(O) are known to influence the probability of this effect.[28] When the procedure illustrated in Scheme 3 was applied to cyclohexyl propionate, $ROC^*(O)CH_2CH_2(H)^\gamma$, and dicyclohexyl glutarate, $ROC^*(O)CH_2CH_2(CH_2C(O)OR)^\gamma$, we concluded that the value of $\gamma_{C(O)-CHC(O)OR}$ seemed to be of the same order or even more.

(ii) The chemical shift of the C*(O) group appears to be sensitive to long-range interactions as well. Thus, CH groups α (CH^α) and γ (CH^γ) to the C*(O) group and CH_2 groups in the β-position (CH_2^β) also are influenced by γ-gauche shielding effects. These shielding interactions should reduce the deshielding effects[30] produced by the CH^α and CH_2^β groups at C*(O) (g-1,5 and g-1,6 interactions, respectively) and should intensify the shielding effect produced by the CH^γ group at C*(O) (g-1,7 interaction). Thus, the more g-1,4, g-1,5, g-1,6, and g-1,7 interactions the C*(O) group is experiencing in its average conformation environment, the more shielded

Scheme 5. Structure of Pentads in Terms of the Planar Zigzag Conformation. Observed Carbons are Marked by an Asterisk



the carbon becomes. The observed overall spread of the C*(O) chemical shifts (in an interval of $\Delta\delta \simeq 0.8$ ppm) seems to arise from the long-range interactions g-1,5, g-1,6, and g-1,7. When analyzing the carbonyl region, it seems necessary to take into consideration the spatial position and influence of the side-chain substituents (C(O)OR) six bonds apart from the C*(O) group[31] (see Scheme 5). The shift of the central carbonyl signal in pentads from high to low field (i.e., $\delta_{rmmr} < \delta_{rmmm} < \delta_{mmmm}$) reflects the inversion of the chirality of the α-carbon five bonds apart from the observed carbonyl (it results in the substitution of an r unit on the end of a triad sequence for an m unit).

We note that the methylene carbons of the cyclohexyl ring are sensitive to the configurational isomerism of the PCHA chains. In the spectrum of PCHAIV recorded at 125.7 MHz, the signal of the CH_2^c-group (see Scheme 1) is split into three peaks ($\Delta\delta \simeq 0.2$ ppm) assigned to the triad sequences. The chemical shifts of these peaks increase in the same order as those assigned to the main-chain CH group (i.e., mm < mr < rr). In addition, the signal of the CH_2^b group (see Scheme1) is split into four peaks ($\Delta\delta \simeq 0.25$ ppm) due to the pentad sequences.

The observed sensitivity of the cyclohexyl carbons to stereosequences can be interpreted in the light of the γ-gauche effect method. The CH_2^c and CH_2^b groups mentioned above are known[30] to experience a shielding interaction with the C(O) group, and this interaction seems to be intensified by the γ-gauche effect produced at the C(O) group. The spatial position and influence of the C(O)OR groups neighboring the central cyclohexyl ring can be taken into account as well.

It should be interesting to estimate the influence of the substituent size (S) in polyacrylates upon the carbon signal sensitivity to stereosequences. Data collected in Table 5 clearly show that increasing the size of S results in a greater overall spread of chemical shifts of both the main-chain and carbonyl carbon signals. This observation is probably due to the fact that increasing of size

Table 5. Influence of the Size of the Side-Chain Substituent in Polyacrylates upon Carbon Signal Sensitivity to Stereosequences

side-chain substituent in atactic polyacrylates	overall spread of carbon chemical shifts $\Delta\delta$, ppm: methine region (triad)	methylene region (tetrad)	carbonyl region (pentad)
methyl[a]	0.0	1.0	0.2
ethyl[b]	0.5	2.0	
butyl[b]	0.5	2.5	
2-ethylhexyl[b]	0.5	3.0	
isopropyl[a]	0.6	3.2	0.4
cyclohexyl	0.9	4.5	0.8

[a] Matsuzaki.[7] [b] Suchoparek.[11]

of S leads to the increase of the fractional contribution of conformations which do not involve the severe steric hindrance of substituents.[20] Thus, the conformation distribution for each sequence (triad, tetrad, and pentad) seems to become narrower (as in PVC[20,24, 29]), and this fact appears to result in greater carbon signal sensitivity to stereosequence.

Conclusions

The stereochemical structure of PCHA was analyzed not only by classical one-dimensional ^{13}C NMR spectroscopy (by comparison of the experimental intensities with those calculated for PCHA prepared under different polymerization conditions) but also by two-dimensional HMQC NMR spectroscopy. The attempt to apply the γ-gauche effect method to the analysis of stereosequence-dependent chemical shifts in the carbon spectra of the methine, methylene, and carbonyl regions in general has met with considerable success, though due to the bulky C(O)OR substituents, PCHA can be considered to be a sterically crowded polymer, characterized by the conformational and therefore configurational sensitivity of the backbone and side-chain geometry,[32] which happen to override the γ-gauche effect. It was established that increasing substituent size results in a greater carbon signal sensitivity to stereosequence. From the intensities of the triad signals, we found that the chain propagation of PCHA prepared by anionic polymerization with *n*BuLi as catalyst cannot be described by Bernoullian statistics (unlike poly(butyl acrylate) and poly(ethylhexyl acrylate) prepared by group transfer polymerization in THF[11]). The analysis of the triad signals also demonstrated that for PCHA prepared by anionic polymerization at −82 °C, the isotactic extent increased in the order toluene < THF, *n*BuLi < PhMgBr. From the intensities of the tetrad signals it was established that chain propagation of PCHA prepared under different polymerization conditions can be described by first-order Markov statistics (with a tendency toward isotactic structures for PCHA prepared by anionic polymerization and a tendency toward syndiotactic structures for PCHA prepared by radical polymerization). The most considerable deviation from these statistics (Ω = 1.13) is observed for PCHAII, prepared by anionic polymerization in THF.

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