^{1}H and ^{13}C Nuclear Magnetic Resonance Studies on the Stereochemical Configuration of Bis(*N*,*N*-dimethyl-2,4-dimethylglutarylamide) and Poly(*N*,*N*-dimethylacrylamide)

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ABSTRACT: The conformation and configuration analysis of the dimer bis(*N*,*N*-dimethyl-2,4-dimethylglutarylamide) was carried out by means of both conventional ^{1}H and ^{13}C NMR spectroscopy and advanced (INEPTLR and 2D HETCOR) methods. The γ-gauche effect method appears to reproduce the observed chemical shift difference between *m*- and *r*-isomers. Stereochemical structure of poly(*N*,*N*-dimethylacrylamide) (PDMAA) was studied using proton spectrum (at the triad level) and DEPT spectra (at the triad and pentad level). For PDMAA prepared by radical polymerization, the Bernoullian statistics are required to fit the observed intensities at the pentad level.

Introduction

Phase transition and critical phenomena in polymer gels have attracted much attention because of their scientific and technological significance.[1,2] Polyacrylamide and N-substituted polymers proved to be of particular interest due to their unique thermal response in aqueous medium:[1,3,4] phase transition accompanied by a reversible, discontinuous volume change in response to infinitesimal changes in the environmental conditions (temperature, solvent composition).

It has been noticed that detailed chemical structures of polymers (both chemical structure of side chains and stereochemical configuration of main chains) play a vital role in determining the phase behavior of the gel, for example, phase transition temperature.[5] Therefore, the microstructure analysis of the polymer chains is very important.

Polyacrylates have been the subject of many NMR studies by both ^{1}H[6−9] and ^{13}C[10−15] spectroscopy, the latter proving to be more efficient due to its large chemical shift range and therefore greater sensitivity to structure details. However, in spite of the efficient, advanced technique application, the microstructure studies of polymers still meet with considerable difficulties. The stereoregularity investigation of low molecular weight compounds, reproducing dyad and triad segments in the polymer chain, provides information on the preferred conformations of these segments and facilitates the estimation of the monomer distribution character and stereochemical arrangement of various groups in the polymer chain.[16−18] The first study of the stereochemical structure of polyacrylamide derivative poly(*N*,*N*-dimethylacrylamide) (PDMAA) was made by Ba-Gia[19] and Huang[20] but mainly at dyad and triad levels, and the goal of the present investigation was to carry out the detailed microstructure analysis of this polymer and that of the low molecular weight compound bis(*N*,*N*-dimethyl-2,4-dimethylgutarylamide) (DMGA) (modeling dyad sequences in the PDMAA chain) by means of conventional and advanced NMR experiments.

Experimental Section

Model Compounds. Bis(*N*,*N*-dimethyl-2,4-dimethylglutarylamide) (DMGA) was prepared by the reaction of 2,4-dimethylglutaroyl chloride with dimethylamine in solution of dry diethyl ether at room temperature. The crude amide was purified by fractional distillation at reduced pressure (bp 120 °C, 0.1 mmHg). *N*,*N*-Dimethylacrylamide (DMAA) was supplied by Aldrich Co.

Polymer: Poly(*N*,*N*-dimethylacrylamide) (PDMAA). DMAA was polymerized by free radical polymerization in dimethylformamide (DMF) solution at 50 °C under high vacuum. 2,2′-Azobis(isobutyronitrile) (AIBN) was used as initiator, $[\mathrm{I}] = 1.25\ \mathrm{mol \cdot L^{-1}}$. The homopolymer was isolated by precipitation of the reaction mixture in a large excess of diethyl ether. A conversion higher than 85 wt % was reached after 6 h of the reaction. The number-average molecular weight (M_n) determined by SEC (using DMF and PMMA standards) was found to be 62 000 with polydispersity index $M_w/M_n = 2.3$.

NMR Measurements. ^{1}H and ^{13}C NMR spectra of the model compound DMGA were recorded on a Varian Unity-500 spectrometer (operating at 499 and 125.7 MHz for ^{1}H and ^{13}C NMR frequencies, respectively) at 30 °C using 15% (w/v) solutions in $CDCl_3$. Model compound was also investigated by the application of 2D HETCOR spectroscopy (two-dimensional heteronuclear (^{13}C−^{1}H) correlation)[21] and the INEPTLR (long range insensitive nuclear enhanced by polarization transfer) experiment.[22] When using the 2D HETCOR sequence, a total of 256 scans were accumulated over 128 t_1 increments with a relaxation delay of 1.0 s. The INEPTLR

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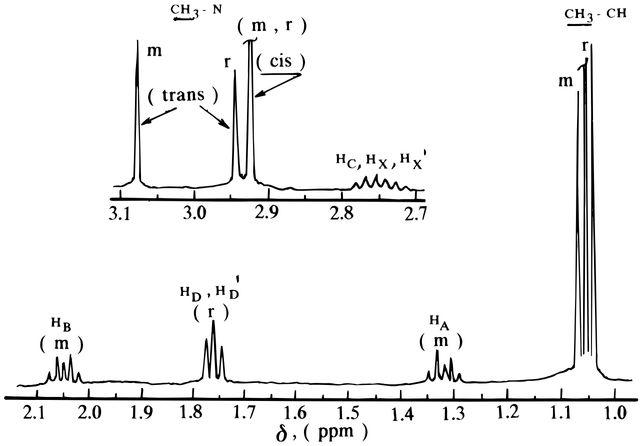


Figure 1. ^1H NMR spectrum of the model compound DMGA.

experiment is a modified version of the original INEPT sequence where all the proton-decoupled pulses are replaced by selective ones. The INEPTLR experiment was carried out by means of the heteronuclear pulse sequence using low-power DANTE-type selective decoupler pulses. The experiment was optimized for 5 Hz couplings with selective excitation of the methylene and N-CH_3 protons in *m*- and *r*-isomers of the model compound (see Figure 1, Table 1, and Scheme l); 1024 transients were used for every spectrum.

One-dimensional ^1H and ^{13}C NMR spectra of PDMAA were recorded on a Varian XL-300 spectrometer at 60 °C using 15% (w/v) solutions in DMSO-d_6. DEPT spectra of PDMAA were obtained in standard conditions with a relaxation delay of 2 s. A value of the C-H coupling constant J_{CH} = 130 Hz corresponding to the dimer model DMGA was considered as the optimum to determine the delay conditions. In order to obtain subspectra of the CH_3, CH_2, and CH groups, we designed four different DEPT experiments (at 45°, 90°, 90°, and 135°) with application of the automatic spectral editing.[23] Solutions of PDMAA in pyridine-d_5 were used for experiments in the Varian Unity-500 spectrometer and DMSO-d_6 for experiments in the Varian XL-300 equipment.

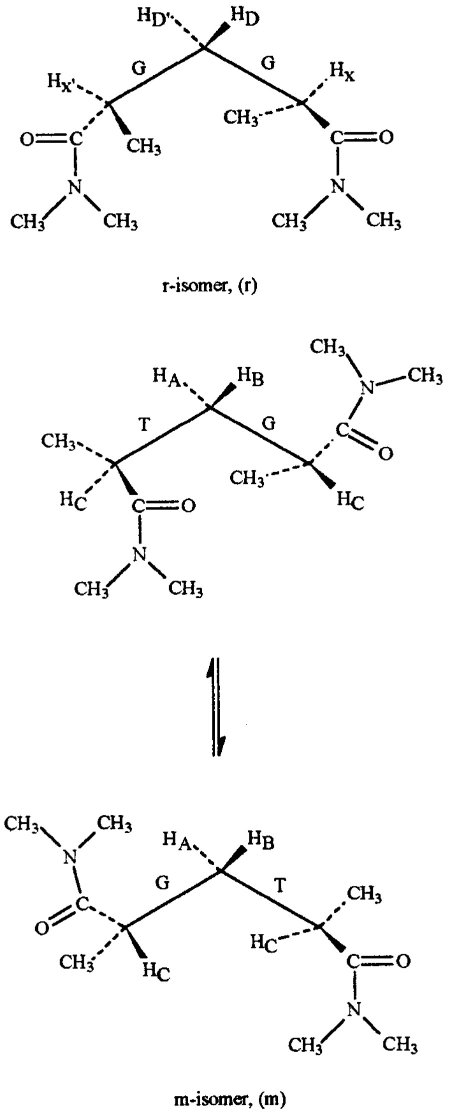
All chemical shifts cited are referred to hexamethyldisiloxane as internal standard.

Results and Discussion

Analysis of Dimer. Conformation population of dyad sequences in the polymer chain can be determined from the coupling constant analysis of the proton NMR spectra of the compounds reproducing the dyad sequences in the polymer chains.[24–26] In Figure 1 the proton NMR spectrum of DMGA (modeling the dyad sequences in the homopolymer chains of PDMAA) is shown. Using this spectrum one can determine the following *J* couplings: J_{BC} and J_{AC} in *m*-isomer by analyzing the splitting of peaks corresponding to H_B and H_A, respectively, both multiplets being the superposition of two triplets ($J_{AC} = J_{BC}$ = 7.5 Hz) separated by 13 Hz (J_{AB}) (spin system ABC_2); J_{DX} and $J_{D'X}$ in *r*-isomer by analyzing the splitting of the peak corresponding to H_D and $H_{D'}$ as spin system DD′XX′ ($J_{DX} = J_{D'X'}$ = 7.0 Hz); and J_{CMe} (in *m*-isomer) and J_{XMe} (in *r*-isomer) by analyzing the splitting of Me signals which are the superposition of two doublets with 7.0 Hz peak separation.

Data of coupling constant analysis (in *m*-isomer $J_{AC} = J_{BC}$ = 7.5 Hz; in *r*-isomer $J_{DX} = J_{D'X}$ = 7.0 Hz) provide information (using Boveys method[24–26]) on the conformer preferences of the dimer: *r*-Isomer exists mainly in GG-conformation, while *m*-isomer exists as an equimolar mixture of energetically equivalent GT- and TG-conformations (see Scheme l). Using relative intensities of the signals H_B, H_D, and H_A, we also calculated the stereoisomer composition of the dimer and found *m* = 56% and *r* = 44%. The assignment of the signals corresponding to the methyl protons of the N-CH_3 groups was made taking into consideration the isomer composition of dimer and the model given by Paulsen and Todt[27] according to which protons of N-CH_3 group cis to oxygen resonate at higher field than those trans to oxygen.

Scheme 1. Preferable Staggered Conformation of *m*- and *r*-DMGA



The carbon spectrum of the dimer is presented in Figure 2. 2D HETCOR spectrum (Figure 3) provides the assignment of the signals corresponding to CH_2, CH, and N-CH_3 groups of *m*- and *r*-isomers. Data of isomer composition (according to which more intense carbon signals are ascribed to the *m*-isomer) should be taken into account. Two nonequivalent CH_2 protons of *m*-isomer (H_A and H_B) give two correlation peaks, a and b, for the respective more intense carbon signal at 37.66 ppm, while equivalent CH_2 protons of *r*-isomer (H_D and $H_{D'}$) give one correlation peak, d, for the respective less intense carbon signal at 38.40 ppm. Methine protons in *m*-isomer (H_c) (known to be less shielded by C(O)OR groups than methine protons in *r*-isomer[24]) give for the respective more intense carbon signal at 32.96 ppm, the correlation peak c shifted (in the proton dimension) to the lower field in comparison with the correlation peak x, arising from methine protons in *r*-isomer (H_x), for the

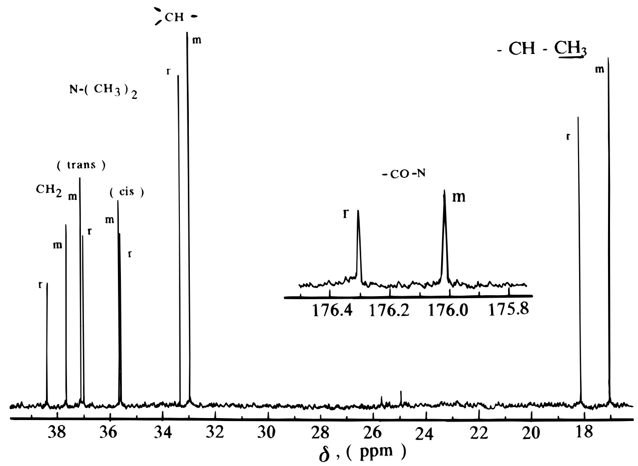


Figure 2. ^{13}C NMR spectrum of the model compound DMAGA.

respective less intense carbon signal at 33.32 ppm. Proton signal of N-CH_3 group at 3.09 ppm corresponding (in accordance with the assignment in proton spectrum) to *m*-isomer gives correlation peak s for the respective more intense peak at 37.11 ppm, while proton signal of N-CH_3 group at 2.94 ppm corresponding to *r*-isomer gives correlation peak l for the respective less intensive peak at 37.02 ppm. The assignment of the signals corresponding to cis and trans methyl (N-CH_3) carbons is made when taking into consideration the shielding proximity effect of the carbonyl group:[28] Carbons that are cis to the carbonyl oxygen are invariably shielded relative to the trans case.

The assignment by means of INEPTLR experiment was carried out using models of the preferable staggered conformers of *m*- and *r*-isomers (Scheme 1) and on the basis that only the carbons having long range interactions with the selectively excited protons will show up in the spectrum due to the polarization transfer from the excited proton spin system to the carbon spin system (Table 1). Thus, data presented in the Table 1 not only argue in favor of the assignment presented in Figures 1 and 2 but also correlate with the results of the conformational analysis made by coupling constant analysis of the proton spectrum.

Thus, the assignment of carbon signals (Figure 2) clearly shows that resonances of the methyl (CH_3-CH), methylene, methine, and carbonyl carbons in the meso isomer are observed at higher magnetic field than the corresponding resonances in the racemic isomer. Note that N-$(CH_3)_2$ groups (in both proton and carbon spectra) in the racemic isomer on the contrary resonate at higher magnetic field than in the meso isomer. This trend probably reflects the fact that in *m*-isomer (unlike *r*-isomer) N-$(CH_3)_2$ groups are experiencing the deshielding effect of the neighboring substituent (C(O)N-$(CH_3)_2$ group) disposed in the space close to N-$(CH_3)_2$ groups.

Chemical shift difference between meso and racemic isomers can be interpreted in terms of the γ-gauche effect method[17,29−32] illustrated in Chart 1. According to this chart, (1) CH groups are experiencing the γ-gauche-shielding effect produced by γ-substituent C(O)R ($\gamma_{\text{CH-C(O)R}}$) with conformation bond probability P_t and by γ-substituent CH_3 ($\gamma_{\text{CH-CH}_3}$) with conformation bond probability P_{g+}; (2) CH_3 groups are experiencing γ-gauche shielding effect produced by γ-substituent CHC(O)R ($\gamma_{\text{CH}_3\text{-CHC(O)R}}$) with probability P_{g+}; and (3) C(O) groups are experiencing γ-gauche-shielding effect produced by γ-substituent CHC(O)R ($\gamma_{\text{C(O)-CHC(O)R}}$) with probability P_t. High-energy state (conformation bond probability P_{g-}) is known to be nearly excluded.[30]

Values of $\gamma_{\text{CH}_3\text{C(O)R}}$ and $\gamma_{\text{C(O)-CH}}$ determined by the procedure illustrated in Chart 2 prove to be close but higher than $\gamma_{\text{C-C}}$ (−5.5 ppm[33]), since the value of P_g for butyramide is considered to be less than that for butane (P_g = 46%[33]) due to more severe overlapping of the bulkier C(O)NH_2 group with CH_3. The results of the application of the γ-gauche effect method for the prediction of the relative chemical shifts of *m*- and *r*-isomers are presented in Table 2. The data shown in this table clearly demonstrate the correlation between estimated and observed chemical shifts only for CH and C(O) groups of the dimer, while for CH_3 groups the significant discrepancy is apparent. Probably, the ^{13}C chemical shift differences between the meso and racemic isomers of the dimer could not be explained only in terms of the conformation difference of the main chain,[16] and for CH_3 groups it is necessary to take into account the spatial position of the neighboring substituents (C(O)R) in *m*- and *r*-isomers (Scheme l). The methylene group of the dimer does not experience the direct γ-gauche-shielding effect, but γ-shielding interactions of the attached CH groups should reduce the deshielding effect[33] produced by this group at CH_2. Keeping in mind the data presented in Table 2 for CH groups, we can conclude that the CH_2 group in *r*-isomer appears to be more deshielded than in *m*-isomer, and this conclusion corresponds to the assignment shown in Figure 2. Methyl (N-CH_3) groups also are not affected by the direct γ-gauche-shielding effect, but γ-shielding interactions of carbonyl groups in β-position to them ($C(O)^{\beta}$) should intensify the shielding effect[34] produced by $C(O)^{\beta}$ groups at N-CH_3. Thus, N-CH_3 groups in *m*-isomer should be shielded more than in *r*-isomer (in accordance with the data presented in Table 2 for C(O) group), but this conclusion does not correlate with the assignment shown in Figure l. Perhaps, the influence of other contributions (solvent effect,[28,31] space vicinity of the neighboring substituents, conformational and therefore configurational sensitivity of the backbone and side chain geometry in this sterically crowded dimer[35]) overide the γ-gauche effect. Thus, we can draw the conclusion that the γ-gauche effect method for calculating ^{13}C chemical shifts reproduces the observed chemical shift difference between *m*- and *r*-isomers for CH, CH_2, and C(O)O groups of the dimer DMAGA.

Homopolymer PDMAA. In the proton spectrum of this homopolymer, only the signal of N-CH_3 protons proved to be sensitive to the configuration isomerism of the polymer chain splitting into three peaks due to triad sequences (Figure 4). The assignment is made in accordance with the proton spectrum of the dimer (region of N-CH_3 groups) (Figure l).

The microstructural analysis of the homopolymer chains by means of the conventional carbon spectrum seems to be unsuccesful due to the severe overlap of the signals of the main-chain carbons and N-CH_3 groups; the carbonyl signal appears to be little affected by the stereoregularity of the chain (Figure 5). Nevertheless carbon spectra recorded by the application of the DEPT sequence enable us to carry out the stereochemical structure study of the homopolymer chains. Possible distortions of signal intensities, arising from the DEPT sequence, can be neglected if these signals correspond to one and the same group.

In the DEPT spectrum of the $N(CH_3)_2$ carbon (Figure 6), one can observe two split signals of equal intensity.

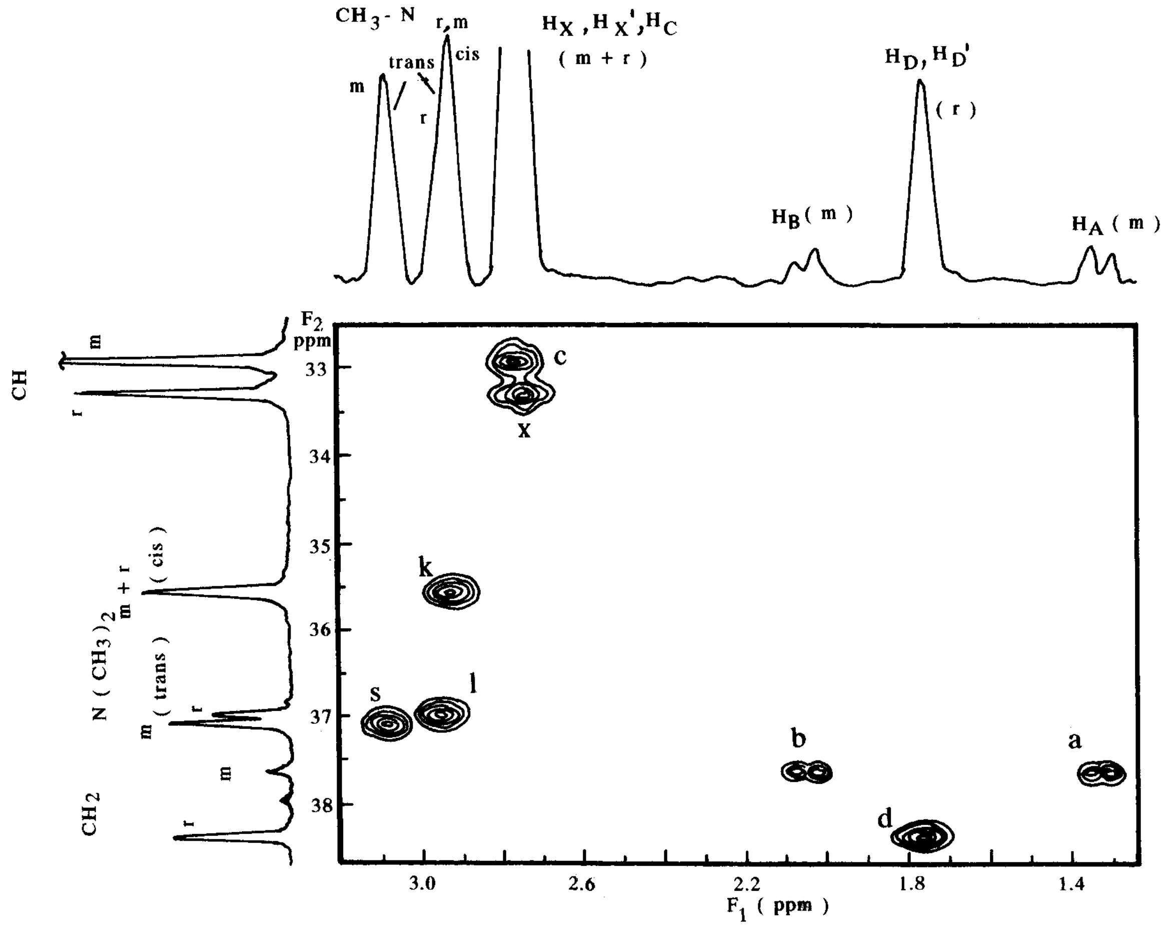
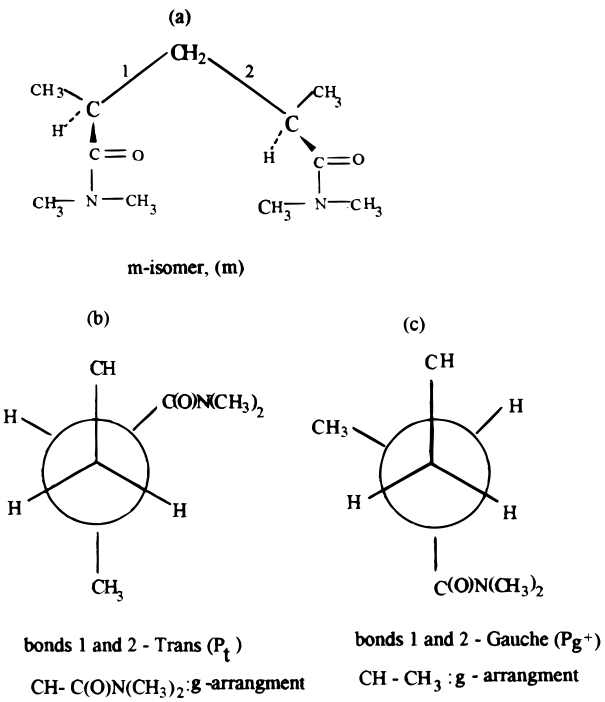


Figure 3. Two-dimensional ($^{13}C-^{1}H$) HETCOR NMR spectrum of the 10% solution of the model compound DMGA in $CDCl_3$, recorded at 30 °C.

Table 1. Carbon Signals Observed in the INEPT Long Range Spectra of the Dimer DMGA

selective irradiation at protons	observed carbon signals in ^{13}C NMR (δ, ppm)			
	CH	CH_3–CH	C=O	CH_3N
CH_2 (*r*) 1.75 ppm CH_2 (*m*)	33.31 (*r*)	18.16 (*r*)	176.30 (*r*)	
H_A (1.32 ppm)	32.96 (*m*)	17.02 (*m*)	176.01 (*m*)	
H_B (2.04 ppm)	32.96 (*m*)	17.02 (*m*)		
NCH_3 (*trans-m*) (3.08 ppm)				35.62 (*cis-m*)
NCH_3 (*trans-r*) (2.94 ppm)			176.30 (*r*)	35.58 (*cis-r*)
NCH_3 (*cis-m* + *r*)				37.02 (*trans-r*)
(2.92 ppm)	32.96 (*m*)		176.01 (*m*)	37.11 (*trans-m*)

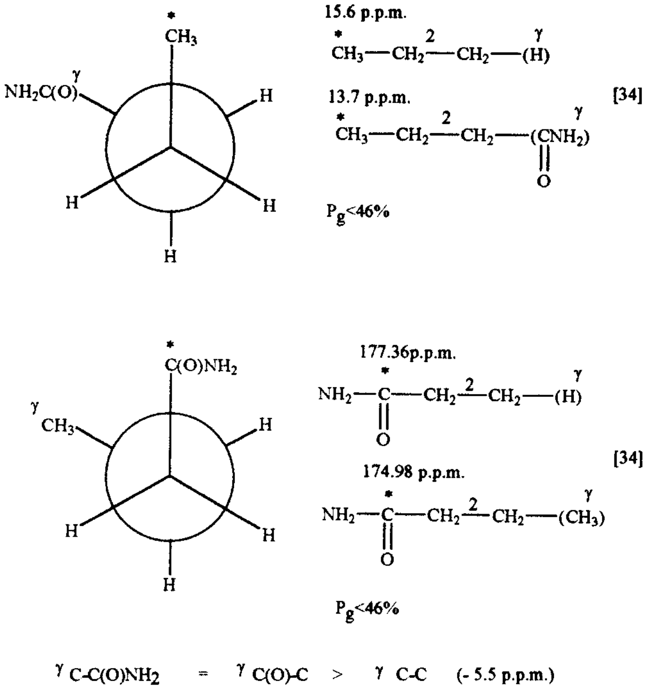
Chart 1



[a] (a) *m*-Isomer of the dimer in all-trans planar zigzag conformation. (b and c) Newman projections along bonds 1 and 2 of the dimer.

In accordance with the carbon spectrum of the dimer (Figure 2), we can ascribe the upper field signal to the NCH_3 carbons in cis and the lower field one to the NCH_3 carbons in trans position with respect to the carbonyl oxygen. Cis NCH_3 group signal seems to be little affected by the stereoregularity of the homopolymer chains and splits into two peaks in an interval of $\Delta\delta = 0.3$ ppm (34.6–34.9 ppm) due to the triad sequences. Trans NCH_3 group signal proves to be more sensitive to the configurational isomerism of the polymer and though it also splits into two peaks, the splitting interval is 2 times as much ($\delta = 0.6$ ppm) and the lower field peak (at 36.25 ppm) appears to have additional splitting reflecting pentad structures. Note that in the carbon spectrum of the dimer (Figure 2), the chemical shift difference between *m*- and *r*-isomers for cis NCH_3 group seems to be less (0.04 ppm) than that for trans NCH_3

Chart 2. Determination of the γ-Gauche-Shielding Effect Produced by γ-Substituents $C(O)NH_2$ and CH_3[a]



[a] Newman projections along two bonds.

Table 2. Correspondence between Observed and Estimated Chemical Shifts in the Carbon Spectrum of the Dimer via the γ-Gauche Effect Method

group	isomer	chemical shift (δ, ppm)	preferable[a] conformation	bond conformation probability		total shielding effect (ppm)[b]
				P_g	P_t	
CH	*m*	32.96	TG−GT	0.5	0.5	−6.0
	r	33.32	GG	1.0	0.0	−5.0
C=O	*m*	176.0	TG ⇄ GT	0.5	0.5	−3.5
	r	176.30	GG	1.0	0.0	0.0
CH_3	*m*	17.02	TG ⇄ GT	0.5	0.5	−2.5
	r	18.16	GG	1.0	0.0	−7.0

[a] By the data of the coupling constant analysis. [b] $\gamma_{C\text{-}C(O)NH_2} = \gamma_{C(O)\text{-}C} = -7.0$ ppm and $\gamma_{C\text{-}C} = -5.0$ ppm are assumed to be applicable.

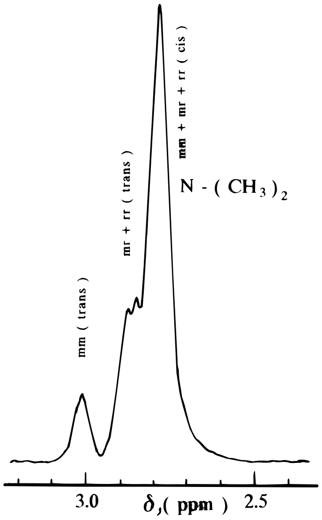


Figure 4. ^1H NMR spectrum (region of the $N(CH_3)_2$ proton signals) of the homopolymer PDMAA, recorded at 125.7 MHz.

group (0.09 ppm). The assignment of $N(CH_3)_2$ carbon signals are carried out (Figure 6, Table 3) by a comparison of the experimental signal intensities with calculated triad populations assuming the Bernoullian statistics and in accordance with the carbon spectrum of the dimer (Figure 2). The spatial position of the substituent $C(O)N(CH_3)_2$ (assumed to produce the deshielding effect at NCH_3 groups) neighboring the central $N(CH_3)_2$ group in different triads must be taken

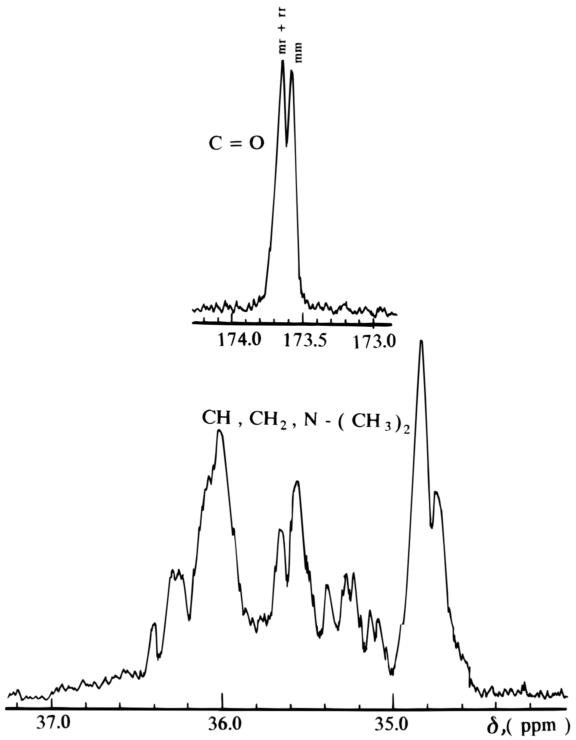


Figure 5. Conventional ^{13}C NMR spectrum of the homopolymer PDMAA, recorded at 125.7 MHz.

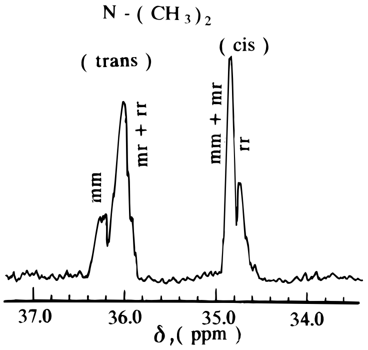


Figure 6. ^{13}C NMR spectrum (region of the $N(CH_3)_2$ carbon signals) recorded using DEPT sequence at 125.7 MHz.

Table 3. Assignment of the ^{13}C NMR Resonance Signals of the $N(CH_3)_2$ Groups for Triad Sequences of PDMAA Chains

integration limits in ^{13}C NMR (δ, ppm)	triad	triad molar ratio	
		expt	calcd[a]
34.6−34.8	cis	0.22	0.17
	rr		
34.8−35.0	cis	0.78	0.35
	mm		0.48
	mr		
35.8−36.2	trans	0.68	0.48
	mr		0.17
	rr		
36.2−36.4	trans	0.32	0.35
	mm		

[a] According to Bernoullian statistics (Bernoullian probabilities $P_m = 0.59$ and $P_r = 0.41$ were determined by means of PDMAA proton spectrum (Figure 4)).

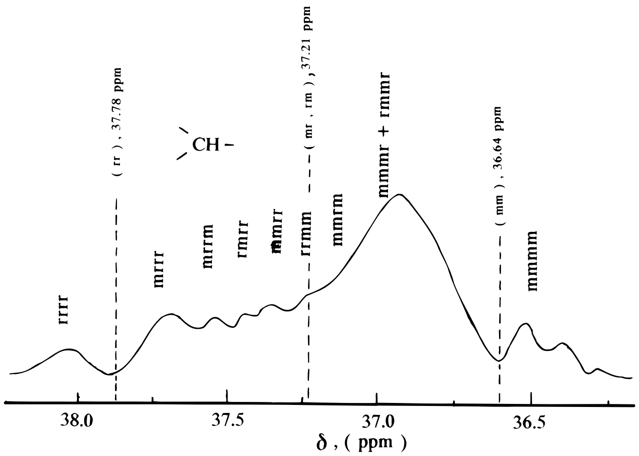


Figure 7. ^{13}C NMR spectrum (region of the methine carbon signals) recorded using DEPT sequence at 50.28 MHz.

into account as well. The assignment of the lower field signal split into three peaks due to pentad sequences to *mm*-triad correlates with the assumption that *mm*-triad is more compressed[31] and therefore more sensitive to the polymer chain stereoregularity. From the DEPT spectrum of the NCH_3 groups using relative signal intensities, one can determine such important characteristics describing the polymer chains as triad molar fraction and conditional probabilities:[14,15] $mm = 0.32$, $rr = 0.22$, $mr = 0.46$, $P_{m/r} = 0.42$, $P_{r/m} = 0.51$. These data show that the chain propagation of PDMAA prepared by the radical polymerization slightly deviates from the Bernoullian statistics ($P_{m/r} + P_{r/m} = 0.93$).

In the DEPT spectrum of the methine region (Figure 7), one can observe the splitting of the CH group signal into at least five peaks in an interval of $\Delta\delta = 1.9$ ppm (36.3−38.2 ppm) due to pentad sequences. Keeping in mind that in the carbon spectrum of the dimer CH groups in *m*-isomer are more shielded than in *r*-isomer (Figure 2), we can ascribe the peak at the highest field (36.46 ppm) to the pentad with the central *mm*-triad and the peak at the lowest field (37.98 ppm) to the pentad with central *rr*-triad. Noteworthy is the peak at 36.46 ppm which appears to split into two additional peaks. This observation is probably due to the fact that this pentad is more compressed and the methine carbon may be more sensitive to the configuration of the monomer on each end of the pentad, i.e., to heptad structure. The tetrads *mmm*, known to be more compressed than other tetrad sequences due to its preferred helix (rather than a planar zigzag[31]), correlate with two pentads—*mmmm* and *mmmr*. A comparison of the experimental signal intensity (at 36.46 ppm) with calculated pentad *mmmm* and *mmmr* populations assuming Bernoullian statistics argues in favor of *mmmm* pentad. Thus, the shift of the central methine carbon signal in pentads from high to low field (i.e., $\delta_{mmmm} < \delta_{mmmr}$, etc.) reflects the inversion of the chirality of the α-carbon (four bonds removed from the observed carbon) that results in the substitution of *m*-unit on the end of the triad for *r*-unit. The assignments of pentads based on this trend are presented in Table 4 and Figure 7. This pentad assignment seems to be conclusive not only because of the good agreement between the experimental and calculated pentad contents but also because of the fact that chemical shifts of triad sequences determined in accordance with the pentad assignment ($\delta_{mm} = 36.64$ ppm, $\delta_{rr} = 37.78$ ppm, $\delta_{mr} = 37.21$ ppm) submit to the additive scheme $\delta_{mm} + \delta_{rr} = 2\delta_{mr}$. This rule of the chemical shift equality of homo- and heterotriad signals is known to be a useful criterion for the correct signal assignment.[30,31]

Table 4. Assignment of the ^{13}C NMR Resonance Signals of the Main-Chain CH Group for Pentad Sequences of PDMAA Chains

		pentad molar ratio		
			calcd[a]	
integration limits in ^{13}C NMR (δ, ppm)	pentad	expt	assuming Bernoullian statistics	assuming first-order Markov statistics
36.3−36.6	*mmmm*	0.08	0.10	0.10
36.6−36.9	*mmmr*	0.73	0.16	0.14
	rmmr		0.06	0.05
36.9−37.45	*mmrm*		0.17	0.13
	mmrr		0.13	0.12
	mrmr		0.13	0.10
	rmrr		0.10	0.10
37.45−37.80	*mrrm*	0.15	0.05	0.06
	mrrr		0.08	0.12
37.80−38.2	*rrrr*	0.04	0.04	0.06

[a] Bernoullian probabilities ($P_m = 0.56$, $P_r = 0.44$) and conditional probabilities ($P_{m/r} = 0.42$, $P_{r/m} = 0.51$) determined from the DEPT spectrum of the NCH_3 groups (Figure 6).

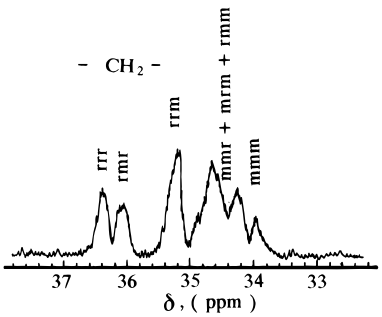


Figure 8. ^{13}C NMR spectrum (region of the methylene carbon signals) recorded using DEPT sequence at 125.7 MHz.

In the DEPT spectrum of the methylene region (obtained as the combination of S1−S4, where S1is the DEPT spectrum with all the protonated carbon signals and S4 is the DEPT spectrum with methyl carbon signals), one can observe the splitting of CH_2 group signal in an interval of $\Delta\delta = 2.3$ ppm (34.0−36.5 ppm) due to tetrad sequences (Figure 8). Keeping in mind that in the carbon spectrum of the dimer reproducing the dyad sequences in the PDMAA chains, the CH_2 group in *m*-isomer is shielded more than in *r*-isomer, and in accordance with the tetrad analysis of the other polyacrylates,[14,15] we can suggest the following order of the tetrad signals as *rrr*, *rmr*, *rrm*, and *mmr* + *mrm* + *mmm* from low to high field.

Conclusions

The stereochemical configuration of the dimer DMGA was studied by both the conventional ^{1}H and ^{13}C NMR spectroscopy and advanced NMR methods—2D HETCOR spectroscopy and INEPTLR experiment. Coupling constant analysis of the proton spectrum showed that *m*-isomer existed as an equimolar mixture of the energetically equivalent GT- and TG-conformers and the most stable conformation for *r*-isomer should be the GG-conformation. Analysis of the carbon spectrum revealed that the methyl (CH_3-CH), methylene, methine, and carbonyl carbons in the *m*-isomer resonated at higher magnetic field than in the *r*-isomer, and on the contrary NCH_3 groups (in both the proton and carbon spectra) in *r*-isomer are more shielded than in *m*-isomer. The γ-gauche effect method for calculating ^{13}C chemical shifts reproduces observed chemical shifts difference between *m*- and *r*-isomers for $CHCH_2$ and C(O) groups of the dimer. However, for methyl groups (for both CH_3-CH and CH_3N), significant discrepancy appeared to be apparent, probably due to the influence of other contributions overriding the γ-gauche effect.

Stereochemical configuration study of the homopolymer chains was carried out by ^1H and ^{13}C NMR spectroscopy. Proton spectrum enabled us to analyze the microstructure only at the triad level. Conventional carbon spectrum does not provide any information upon chain stereoregularity because of the severe overlap of the signals of the main-chain and side-chain NCH_3 carbons. Carbonyl signal appears to be little affected by the polymer stereoregularity. Application of the DEPT sequence with the automatic spectral editing enables us to study the stereochemical configuration at the triad and pentad levels. From the intensities of triad signals, it was established that the chain propagation of PDMAA prepared by radical polymerization can be described by Bernoullian statistics.

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