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Microstructural analysis of *p*-acryloyloxy-acetanilide and *N*,*N*-dimethylacrylamide copolymers of biomedical interest by NMR

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Abstract

Copolymers with anti-thrombogenic properties based on *N*,*N*-dimethylacrylamide (A) and para-acryloyloxyacetanilide (B) were prepared by radical polymerization in DMF solutions at 50°C using 2,2′-azobisisobutyronitrile (AIBN) as initiator. The reactivity ratios of both monomers were determined by the application of the non-linear least-squares method suggested by Tidwell and Mortimer. The obtained results ($r_A = 0.47$ and $r_B = 0.63$) confirm that this comonomer pair polymerizes statistically but with a moderate tendency to form alternate sequences, depending on the composition of the monomer feed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Reactivity ratios; Copolymer chain microstructure; NMR spectroscopy

1. Introduction

Copolymers of *p*-acryloyloxyacetanilide (an acrylic derivative of *paracetamol*) and *N*,*N*-dimethylacrylamide have been shown to have a promising anti-thrombogenic behavior [1]. However, thrombus formation on polymer surfaces is a complicated process with multiple factors involved. The nature of the polymer surfaces controls protein adsorption and the adsorbed proteins determine the platelet adhesion. It was indicated [1] that the non-thrombogenicity of the A-co-B systems depends on the presence of hydrophilic/hydrophobic domains and therefore on the detailed chemical structure of polymers (both chemical structure of side chains and the microstructure of main chains). NMR spectroscopy has proven to be the most effective technique in chemical structure characterization, which not only permits the determination of the copolymer composition and thus the reactivity ratios [2–7] but also provides information on detailed microstructure of the copolymer chains [4,5,8–11]. The goal of the present work is to use NMR data for the analysis of copolymer reactivity ratios and microstructure of the copolymer chains.

2. Experimental

2.1. Monomers

p-acryloyloxyacetanilide (B) was prepared by the reaction of *p*-hydroxyacetanilide (paracetamol) with acryloyl chloride in 5% aqueous sodium hydroxide solution at 0°C according to the method described for the synthesis of the methacrylic analog [12], for which a 50%. yield was obtained.

The *N*,N-dimethyl-acrylamide (A), supplied by Aldrich, was distilled under reduced pressure and the fraction with a b.p. 28°C/5mm–30°C/5 mm Hg was collected.

2.2. Polymerization

Polymerization and copolymerization reactions of A and B were carried out at 50°C, in a thermostatic bath regulated with a precision of 0.1°C, using azobisisobutyronitrile (AIBN) ($[I] = 1.5 \times 10^{-2}$ mol/l) as initiator and dimethylformamide (DMF) as solvent ($[M] = 1.0$ mol/l). All experiments were carried out in Pyrex glass ampoules sealed at high vacuum. After the desired time the reaction mixture was added into a large excess of diethylether and the precipitated polymers were washed with the precipitant reagent and dried at reduced pressure until a constant weight was attained.

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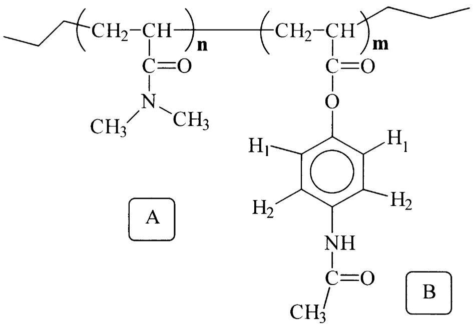


Scheme 1.

2.3. NMR measurements

^{1}H and ^{13}C NMR. spectra of homopolymers (poly-A and poly-B) and of copolymers A-co-B were recorded on a Varian XL-300 spectrometer at 60°C using 5% and 15% (w/v) solutions, respectively, in DMSO-d_6 for homopolymers and in $CDC1_3$ for copolymers. An inverse gated decoupling sequence pulse with a flip angle of 80° (pulse width of 13 μs), and a relaxation decay of 4 s were used.

3. Results and discussion

The chemical structure of the copolymer chains is outlined in Scheme 1. The composition of (A/B) copolymers was determined from the relative intensities of $N(CH_3)_2$ (A-unit) and C_6H_4NH (B-unit) proton resonances (see Scheme 1 and Fig. 1). The molar fraction in the feed and in the copolymer samples for various A/B copolymers are given in Table 1.

The reactivity ratios of monomers A and B (r_A and r_B), were determined according to the general copolymer composition equation using the non-linear least-squares method suggested by Tidwell and Mortimer [13], in which $r_A = 0.47$ and $r_B = 0.63$. The 95% posterior probability contour (PPC) obtained for the A/B comonomer pair is shown in Fig. 2. Hence, both $r_A$and r_B values proved to be less than 1 indicating that neither the A nor the B units have a clear tendency to form blocks in the copolymer chains. The reactivity of growing radicals with A-ends seems to be higher towards *p*-acryloyloxyacetanilide (B) than towards *N*,*N*-dimethylacrylamide (A) monomer molecules ($1/r_A = 2.13$). The growing radicals with B-ends also appear to be more reactive in favor of the cross-propagation with respect to the homopolymerization process (but to a lesser extent as $1/ r_B = 1.49$).

A comparison of the theoretical composition curve obtained from the terminal model copolymer equation [14] using $r_A = 0.47$ and $r_B = 0.63$ with the experimental points (Fig. 3) shows that in the whole range of monomer feed composition the experimental composition data fit adequately the theoretical composition diagram. Moreover, the system A–B is characterized by the azeotropic composition (at $F_A = f_A = 0.40$) and shows a slight tendency towards alternation.

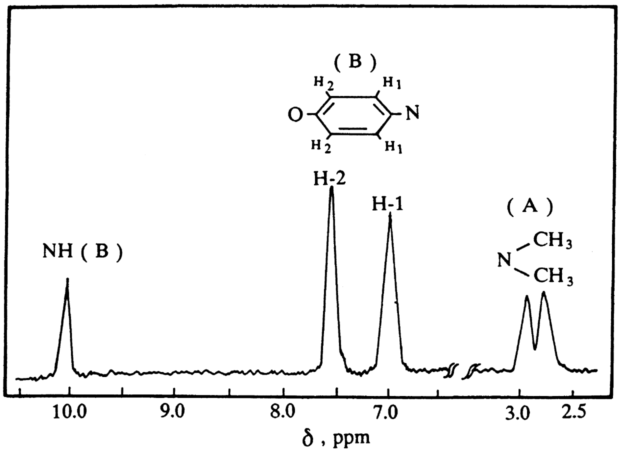


Fig. 1. Expansions of the ^{1}H NMR spectrum of A–B copolymer (F_A = 15 mol%) in $CDC1_3$ at 60°C, corresponding to $N(CH_3)_2$ of A and to the NH and aromatic protons of B. Proton designation is as given in Scheme 1.

Table 1
Feed and copolymer A molar fractions and variation of the random and experimental values of the run number

Molar fraction in feed, F_A	R_{expt}[a]	Molar fraction in copolymer[b], f_A	R_{random}[a]
15	34.0	20	32.0
30	53.2	32	43.5
50	63.4	47	49.8
70	59.2	62	47.1
85	41.7	77	35.0

[a] Calculated using the relationships reported by Harwood [15].
[b] Calculated from the proton spectra.

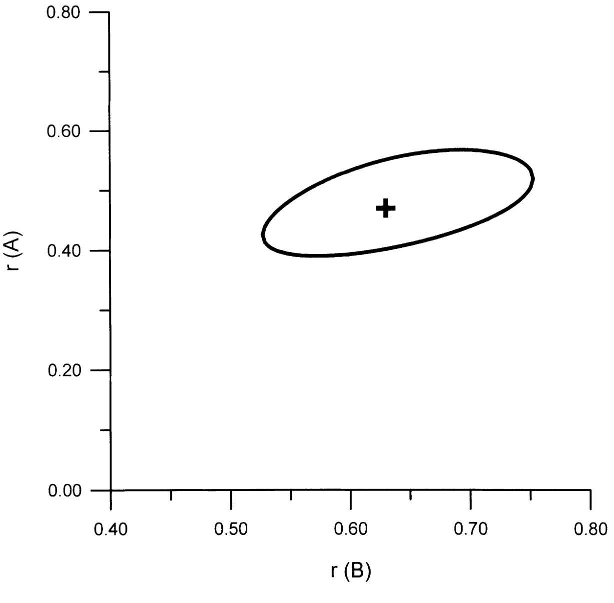


Fig. 2. The 95% posterior probability contour (PPC) for A–B comonomer pair. The (+) represents the best estimated values of r_A and r_B.

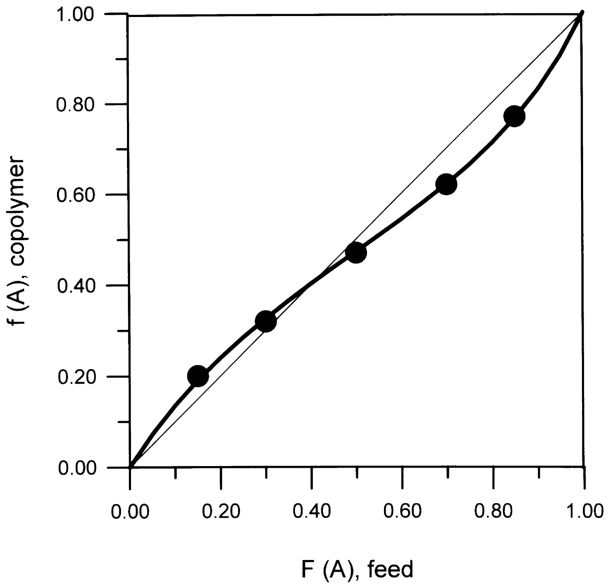


Fig. 3. The theoretical composition curve obtained from the terminal model copolymer equation using $r_A = 0.47$ and $r_B = 0.63$ along with experimental points (●).

Harwood and Ritchey [15] proposed a convenient parameter which provides a useful mental picture of the sequence distribution. The average number of alternating runs (or sequences) occurring in a copolymer per 100 monomer units is termed the ''run number'' R. The values of the run numbers for polymers having monomer units distributed randomly along polymer chains (R_{random}), and experimental run numbers of polymers formed instantaneously from a given polymerization mixture (R_{expt}) are given in Table 1. These data clearly show that $R_{\mathrm{expt}} > R_{\mathrm{random}}$, thus reflecting that the monomer units tend to alternate in the copolymer. The maximum number of alternating sequences ($R_{\mathrm{expt}} = 63.4$) is observed for equimolar monomer feed composition.

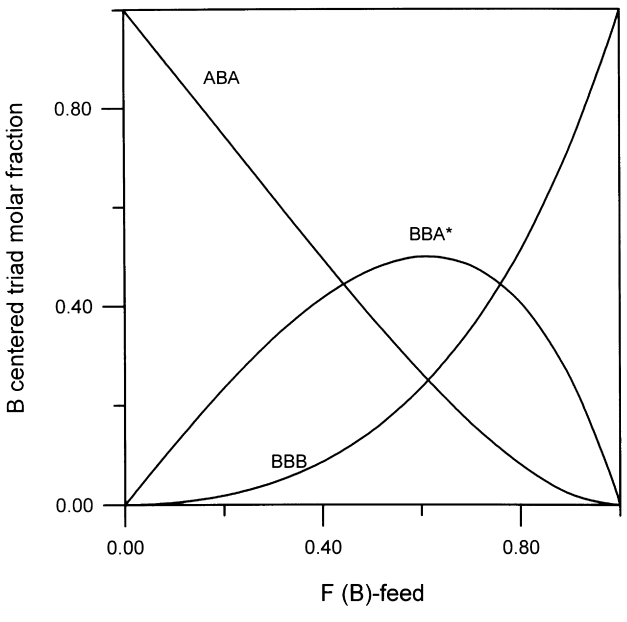


Fig. 4. Plots of the calculated B-centered triad fractions versus the B feed molar fraction F_B.

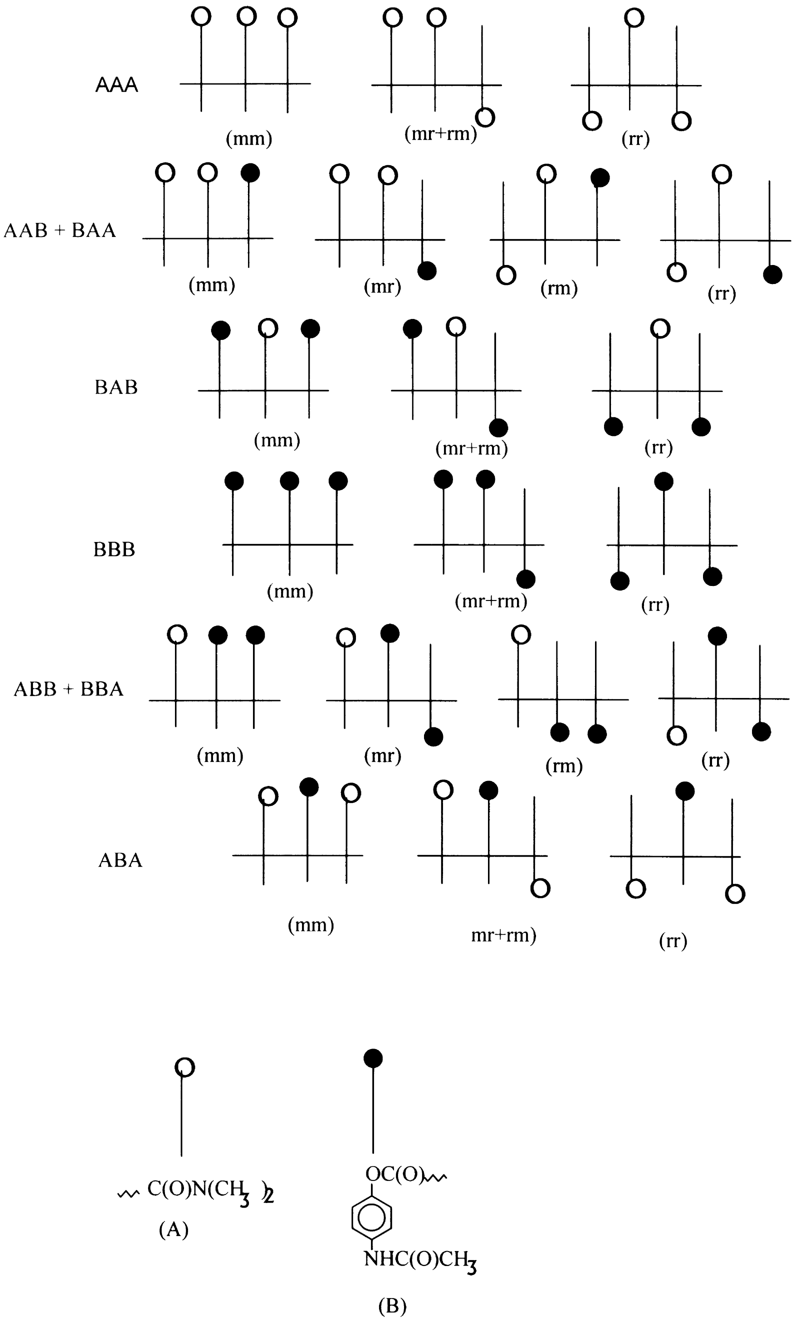
Thus, the analysis of reactivity ratios indicates that the copolymer system *p*-acryloyloxyacetanilide (A) – *N*,*N*-dimethylacrylamide (B) tends to have more alternating distribution of monomer units. This fact probably reflects some dipolar interactions between the acetamido group linked to the aromatic ring of B-monomer and *N*,*N*-dimethylamide groups of A-monomer. These interactions seem to result in true molecular complexes which considerably affect the acrylic double bond of the interacting species [6,16].

On the basis of well-known statistical equations [17] and using the obtained values of reactivity ratios ($r_A = 0.47$ and $r_B = 0.63$) one can determine (assuming a first-order Markov model) such important characteristics describing the copolymer chains as conditional probabilities (P_{AA}, P_{BB} and P_{AB}) and molar fractions of triads with A- or B-central units. Fig. 4 shows the diagrams of the statistical distribution of B-centered triads along the copolymer chains as a function of F_B, the B feed molar fraction. As expected [4,6] the ABA triad content decreases drastically whereas the content of the homotriad BBB increases smoothly with increasing F_B. However, the molar fraction of heterotriads having one A unit, BBA* = BBA + ABB passes through a maximum of $F_B = 0.6$.

3.1. Microstructure determination of A–B copolymer

The copolymer chains can be described by six composition A- and B-centered triads with relative configuration sequences: coiso (mm), cohetero (mr + rm) and cosindiotactic (rr) triads (as shown in Scheme 2).

^{1}H NMR studies: Fig. 5 presents the ^{1}H NMR spectra of the N(CH_3) groups of the A-units of several A–B copolymer samples with various compositions together with that of the A-homopolymer. The signal of $N(CH_3)_2$ groups (proved to be the most sensitive to the microstructure of copolymer chains) is observed in an interval of $\Delta\delta = 0.6$ ppm (2.60–3.20 ppm) and splits into two main peaks. The intensity of the lower field peak decreases whereas the intensity of the upper field one increases with increase in the monomer B concentration in the feed. In a previous article we have considered these signals for homopolymer A samples, as well as for the dimer model compound, to be assigned according to the relative spatial orientation of the N–CH_3 group with respect to the carbonyl amide function [18]. The results obtained demonstrated that the ^{1}H-resonance signal of the N–CH_3 group in *meso*, m, sequences and with isomeric *trans*-position with respect to the carbonyl amide group, are deshielded with respect to the same group in *r* sequences or in isomeric *cis* orientation. We consider that this criterion can be applied in the case of copolymers A–B, as the diamagnetic effect of the carbonyl ester groups of B units in the neighborhood of the A units is rather similar to



Scheme 2.

that of the neighboring carbonyl amide function of sequences of A units.

Therefore, the assignment of the signals (Table 2) was carried out taking into consideration the following criteria:

- A comparison of the copolymer spectra with different values of *f*.
- A comparison of the experimental signal intensities with calculated centered triad populations, assuming a first-order Markov model [17].
- A proton spectra of the homopolymer poly-A (Fig. 5,$f_B = 0$) according to which $N(CH_3)_2$ groups in mm-triad are deshielded more than in mr- and rr-triads [18].
- A model given by Paulsen and Todt [19], postulating the protons of NCH_3 group *cis* to oxygen to resonate at a higher field than those *trans* to oxygen (see Structure A of Scheme 1).

According to Bovey [20], Coleman [21], Roussel [16], Ito [22] the population of the stereochemical configuration isomers of A- and B- centered triads (Scheme 2) can be calculated (assuming Bemoullian statistics) on the basis of the isotacticity parameters σ_{AA}, σ_{BB}, σ_{AB} and σ_{BA}, where σ_{ij}

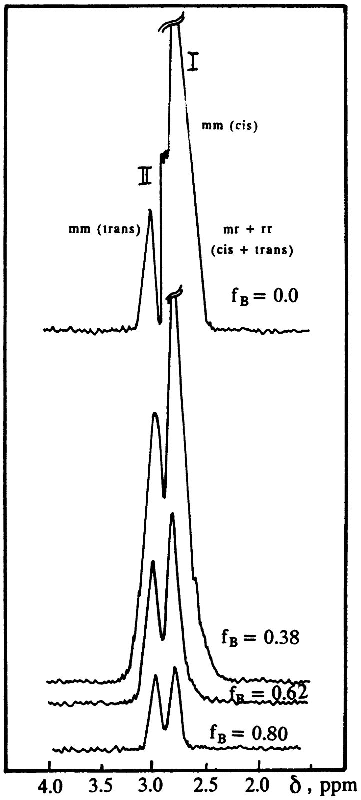


Fig. 5. ^{1}H NMR spectra (300 MHz) of the $N(CH_3)_2$ groups of A-units in A–B copolymers.

is the probability of generating a *meso* dyad between an *i* ending growing radical and incoming *j*-monomer. The values of σ_{AA} and σ_{BB} were determined from the proton spectra of homopolymers poly-A and poly-B, as 0.59 and 0.52, respectively. Assuming that $\sigma_{AB} = \sigma_{BA} = \sigma^*$ [13,21], we have determined this parameter by a comparison of the experimental intensity of the peak S_{II} corresponding to isotactic isomers of A-centered triads (see Table 2) with calculated (by application of well known statistical relations [13,19,21,17]) triad population for several copolymer samples. The obtained average value of $\sigma^* = 0.85$ indicates that the isotactic placement is favored for the A–B system. Similar results have been obtained for other monosubstituted vinyl copolymer systems such as styrene methylacrylate, $\sigma^* = 0.80$ for the radical polymerization at 60°C, and $\sigma^* = 0.85$ for the polymerization at −25°C under γ-radiation [22]. The coisotactic parameter is known to reflect interactions between the substituents of different monomer units. These interactions depending on both steric and polarity factors, play a major role in the stereochemical control of the growing radicals [22]. Keeping in mind that these interactions favor the formation of isotactic segments [16], we can conclude that such a high value of σ^* provides the support for the strong dipolar interactions operating between the acetamido group linked to the aromatic ring of B-units and the *N*,*N*-dimethylamide group of the A-monomer. The data in Table 2 show that the proton spectra of the copolymer systems are little affected by the compositional structure of copolymer chains, but that the spatial interaction of neighboring units or that between the side groups of A or B radical ends and the corresponding incoming monomer units, modify the magnetic character of the $N–CH_3$ groups.

^{13}C NMR Studies: Fig. 6 shows the spectra of the amide carbonyl resonances for four copolymer samples of different composition together with those of the corresponding A and B homopolymers. The amide carbonyl resonances of both A and B units present a complex pattern with 14 distinguishable peaks (in an interval of $\delta = 1.21$ ppm) whose intensities change with the average composition of copolymer chains.

A comparison of the copolymer spectra with those of homopolymers makes it clear that peak 2 (its intensity decreases with an increase in f_A) can be ascribed to the homotriad BBB and peaks 13 and 14 (whose intensities increase with an increase in f_A) to mm and mr + rr configuration triads (respectively) in the composition homotriad AAA [4].

The appearance of new 11 signals in the spectra of the copolymers designated 1, 3–12 which were not observed in the spectra of the homopolymers (see Fig. 6) indicates that amide carbonyl signals of A and B units seem to be affected by the configuration and composition isomerism of the copolymer chains. On discussion of the results, the C(O) groups of the central A- and B- units of the compositional sequences were designated as $C(O)^*_A$ and $C(O)^*_B$ respectively.

An analysis of Fig. 6 enables us to draw two conclusions:

(a) The C(O) groups of homopolymer A resonate at a lower magnetic field than those of homopolymer B.
(b) All new signals (except peak 1) are shifted toward a lower field with respect to the signal of homopolymer B

Table 2
Assignment of the ^{1}H-NMR resonance signals of the $N(CH_3)_2$ groups for A-centered triads

Spectral signal number	Integration limits in ^{1}H, δ ppm	Triads with central A unit	
		Compositional	Configurational
I	2.60–2.85	XAX[a]	mm (*cis*), (mr + rm + rr) (*cis* + *trans*)
II	2.85–3.20	XAX[a]	mm(*trans*)

[a] X = B or A.

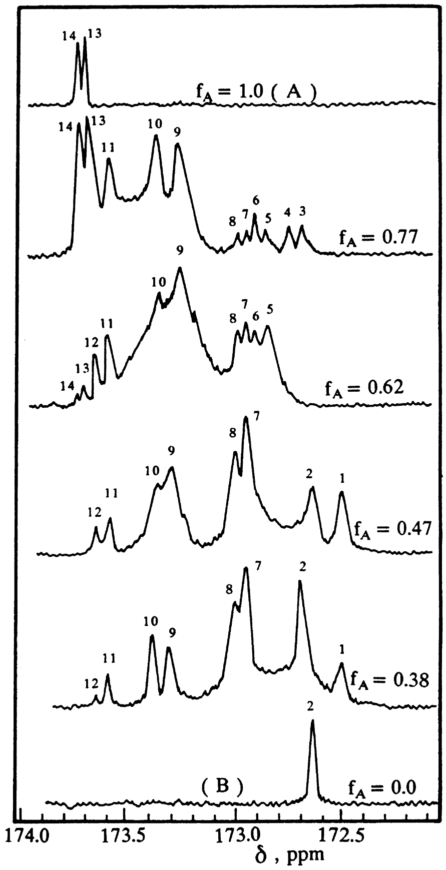


Fig. 6. ^{13}C NMR spectra (75.5 MHz) of the amide carbonyl groups of A–B copolymers.

and toward a higher field with respect to the signal of homopolymer A.

These facts seem to reflect the shielding effect produced by the $C(O)OC_6H_4NHC(O)CH_3$ side group and the deshielding effect produced by the $C(O)N(CH_3)_2$ side group both at the $C(O)^*_A$ and $C(O)^*_B$ (four bonds removed from the respective substituents).

The assignment of compositional A- and B-centered triads were made taking into account the observations mentioned earlier and by a comparison of the experimental signal intensities in the spectra of copolymers of different composition with calculated A- and B-centered triad populations assuming a first-order Markov model [13]. A good agreement between experimental and calculated triad contents not only provides support for the present assignment but also demonstrates that the distribution of the monomer A and B-units in the copolymer chains can be described by the first-order Markov trial. Table 3 shows the calculated and experimental results for several sequences obtained after the analysis of the spectra of two copolymer samples with a high A molar fraction. Using the values of composition triad contents found experimentally one can determine the conditional probability P_{BA} and the number-average sequence length N_A (as $1/P_{BA}$). The values of N_A decrease from 2.94 to 2.22 as the concentration of A in the copolymer increases from a molar fraction of 0.32–0.47. This trend correlates with the fact that the A/B comonomer system has a relatively high tendency towards alternating addition (as was found by the reactivity ratios analysis). The comparison of the chemical shifts of the A- and B-centered homotriad signals with those of heterotriad signals enables us to determine the average shielding effect of substituents α_A and α_B as $\Delta\delta = +0.24$ and $\Delta\delta = 0.16$ ppm, respectively.

However, the spectra of amide carbonyl groups seem to provide information upon the copolymer chain composition microstructure not only at the triad but also at the pentad level. We have tentatively assigned peak 1 (its intensity increases with respect to that of peak 2 in the interval of $0 < F_A < 0.62$, keeping in mind that the $C(O)^*_B$ group in the homopolymer B is not affected by the chain stereoregularity) to the composition B-centered pentad $A^{\beta}B^{\alpha}BB^{\alpha}B^{\beta}$. A comparison of the peak 1 and 2 chemical shifts shows that the substitution of the B-unit in β-position to the central B-unit by the A-unit (or the substitution of the $C(O)OC_6H_4NH$-$C(O)CH_3$ side group six bonds apart from $C(O)^*_B$ for $C(O)N(CH_3)_2$ group) produces a shielding effect at the $C(O)^*_B$ (β_A-substituent effect being $\delta = -0.11$ ppm). Note that the pair of signals 7 and 8 (with a 0.06 ppm peak separation), and assigned to the B-centered heterotriad BBA, practically disappears in the spectrum of the copolymer enriched with the A unit (Fig. 6, $F_A = 0.77$) but instead of this in the higher field one can observe two new pairs of signals (5 and 6; 3 and 4) to compositional pentads with the

Table 3
Assignment of the ^{13}C-NMR resonance signals of the amide carbonyl group for A and B-centered compositional triads and their molar fraction

Peak number	Integration limits in ^{13}C NMR δ, ppm	Composition triad	Molar percentage			
			$f_A = 0.32$		$f_A = 0.47$	
			Expm.	Calcul.[a]	Expm.	Calcul.[a]
1 + 2	172.42–172.56	BBB	26	24	10	7
7 + 8	172.84–172.90	BBA + ABB	35	33	28	25
9 + 10	173.09–173.26	ABA	31	11	44	20
		+BAB		22		22
11 + 12	173.38–173.49	BAA + AAB	8	9	18	20

[a] These data were determined assuming the first-order Markov model (reactivity ratios r_A and r_B as 0.47 and 0.63 respectively).

Table 4
Assignment of the ^{13}C-NMR resonance signals of the amide carbonyl for compositional and configurational sequences

Peak number	Chemical shift, δ, ppm	Compositional sequences	Configuration sequences
1	172.45	ABBB + BBBBA + ABBBA	-−
2	172.56	BBBBB	−
3	172.60	AABBA + ABBAA	mr + rr+ rm
4	172.66		mm
5	172.74	AABBB + BABBA + ABBAB + BBBAA	mr + rr + rm
6	172.80		mm
7	172.84	BBBAB + BABBB	mr + rr + rm
8	172.90		mm
9	173.16	ABA	−
10	173.25	BAB	−
11	173.46	AAB + BAA	mm
12	173.52		mr + rr + rm
13	173.58	AAA	mm
14	173.63	mr + rr + rm	

central ABB triad (designated as T). This pentad assignment seems to be conclusive because of the fact that the chemical shifts of the signals ascribed to pentad sequences ($\delta_{\mathrm{BTB}} = 172.88$ ppm; $\delta_{\mathrm{ATB}} = 172.77$ ppm; $\delta_{\mathrm{ATA}} = 172.63$ ppm) agree with the additive scheme: $\delta_{\mathrm{BTB}} + \delta_{\mathrm{ATA}} = 2\delta_{\mathrm{ATB}}$. This rule of the chemical shift additivity of homo-and hetero sequence signals is known to be a useful criterion for correct signal assignment [17].

The observed splitting (0.06 ppm) between signals 7 and 8, 5 and 6, 3 and 4 (Fig. 6) reveals the sensitivity of the C(O)*$_{\mathrm{B}}$ group in heterotriad ABB to the cotacticity of the copolymer chains. Bearing in mind that the substitution of $\mathrm{C(O)OC_6H_4NHC(O)CH_3}$ group (B-unit) by $\mathrm{C(O)N(CH_3)_2}$ one (A-unit) produces the deshielding effect at the C(O)$_{\mathrm{B}}$ (α_{A}-substituent effect $\delta = +0.24$ ppm) we have tentatively ascribed the low field peaks (4, 6 and 8) to ABB-centered pentads with coisotacic configuration mm (Table 5) in which the deshielding $\mathrm{C(O)N(CH_3)_2}$ group seems to be spatially arranged more closely to C(O)*$_{\mathrm{B}}$ than in mr, rm and rr-isomers [23]. The splitting (0.06 ppm) between peak 12 and peak 11 (corresponding to heterotriad AAB) observed in the spectra of copolymers (see Fig. 6., $0.32 < F_{\mathrm{A}} < 0.77$) could be because of the configuration isomers of heterotriad AAB. The assignment of peaks 11 and 12 to compositional A-centered pentads B$^{\beta}$AABB$^{\beta}$ and A$^{\beta}$AABB$^{\beta}$ is not consistent at least with two factors:

- The intensity of peak 11 does not decrease with respect to that of peak 12 even in the spectrum of the copolymer enriched with A-monomer (Fig. 6, $F_{\mathrm{A}} = 0.62$).
- The β_{A}-substituent effect was found to be shielding (−0.11 ppm).

Taking into account the shielding effect produced by the $\mathrm{C(O)OC_6H_4NHC(O)CH_3}$ group (B-unit) at the C(O)*$_{\mathrm{A}}$ (α_{B}-substituent effect $= -0.16$ ppm) one can predict that the upper field peak 11 and lower field peak 12 correspond to heterotriad AAB with mm and mr +rm + rr configurations respectively (Table 4). The suggested assignment enables us to conclude that the chain of the copolymer enriched with the B-monomer ($F_{\mathrm{A}} = 0.32$) contains composition heterotriads AAB with a predominantly coisotactic configuration. This conclusion correlates with the results obtained by the proton spectra analysis.

Thus, the detailed analysis of the amide carbonyl region of the copolymer spectra reveals the high sensitivity of both C(O)*$_{\mathrm{A}}$ and C(O)*$_{\mathrm{B}}$ groups not only to the composition isomerism but also to the configuration isomerism of the copolymer chains. However an attempt to correlate the molar concentration of the configuration triads with statistical distribution of tacticity has met with considerable difficulties because of small chemical shift differences in signals corresponding to composition and configuration sequences.

In conclusion, the high sensitivity of ^{1}H and ^{13}C-NMR spectroscopy to detect microstructural composition and stereochemical interactions between acrylic co-polymers with highly polar side groups is demonstrated. The NMR results clearly show the strong dipolar interactions between the *N*-methyl groups of the substituted acrylamide units and the aromatic acetamido side group of acrylic ester units. These interactions are responsible for the high value of the coisotacticity parameter $\sigma^* = 0.85$ found for the addition of monomeric units to active radical ends, with a clear tendency to the alternating sequences in a wide range of compositions.

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