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The influence of poly(vinyl alcohol) matrix on stereoregularity of replica polyacrylamide chains in matrix radical graft copolymerization process when varying the grafts number and molecular weight is studied by high-resolution NMR spectroscopy. It was ascertained that the microstructure of formed polymer at homopolymerization and matrix copolymerization processes are not differed. ^{1}H NMR spectroscopy suggests a few contacts of graft chains with the main chain through H-bonding in intramolecular polymer-polymer complex forming in macromolecules of investigated poly(vinyl alcohol)-to-polyacrylamide graft copolymer.

Keywords: graft copolymer; matrix; polymer-polymer complex; replica chain; stereoregularity; structure

INTRODUCTION

Matrix polymerization of synthetic monomers is a process of macromolecules synthesis when the forming polymer chains grow in the contact with matrix macromolecules, which have been introduced beforehand into the polymerization system. The contact of growing polymer chain with matrix is secured with chemical complementation of both macromolecules. The formation of stable cooperative system of intermolecular noncovalent (coulomb or hydrogen) bonds between matrix and replica

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chains is the common property and sign of matrix polymerization. This process results in polymer-polymer complexes (PPC) formation [1].

Poly(vinyl alcohol)-to-polyacrylamide graft copolymers (PVA-*g*-PAA) with chemically complementary main and graft chains, so-called polymer-polymer complexes of intramolecular type, are of great interest as a special type of polymer compounds and as perspective functional materials [2]. The structure and properties of such graft copolymers are monitored by the array of H-bonds that are established between the PVA and PAA and between the neighboring PAA graft chains which relative quantity depends on grafts average number N and length [2–6]. The unique behavior of PVA-*g*-PAA as sensors on low molecular organic compounds [7], as binders of metal ions [8,9], colloid particles [10], cells of living organism and as flocculants [8,10,11] arises from the presence in their structure of both hydrophobic regions and hydrophilic cavities and from the capability to change a hydrophobic-hydrophilic balance in PPC during the sorption or binding processes.

The dynamic and structural effects are known to reveal in matrix copolymerization processes [1,12–15]. The dynamic effect displays in the changing of polymer propagation rate in matrix presence. The structural effect consists in the matrix influence on the molecular weight and microtacticity of growing replica chains. Previously performed investigations of the kinetics of PVA-*g*-PAA copolymerization when varying the grafts average number N and molecular weight have revealed the increase of PAA propagation rate as opposed to homopolymerization in the same experimental conditions (dynamic effect) [16]. So first, it has been demonstrated that radical graft copolymerization is the matrix process. The purpose of this work arises from our interest in matrix (PVA) influence on PAA graft chains stereoregularity, which would allow a better insight into the matrix graft copolymerization mechanism.

EXPERIMENTAL

The following materials have been used for the synthesis of the graft copolymers: (i) poly(vinyl alcohol) with $\overline{M}_v = 80000$ and 13% of residual acetate groups Serva, Sweden; (ii) monomer acrylamide, Reanal, Hungary; (iii) initiator ammonium cerium (IV) nitrate, Aldrich, USA. PVA-*g*-PAA have been synthesized by grafting of polyacrylamide chains onto a poly(vinyl alcohol) backbone using a cerium-ion-initiated solution polymerization technique detailed in our previous paper [17]. A variation on the monomer and initiator concentration has been used to obtain a series of PVA-*g*-PAA samples

TABLE 1 Molecular Characteristics of Graft Copolymers

Name	$\overline{M}_{vPVA} \times 10^{-4}$	$\overline{M}_{vPAA} \times 10^{-5}$	N	$M_{PVA\text{-}g\text{-}PAA} \times 10^{-6}$
PVA-*g*-PAA1	8.0	2.77	28	7.828
PVA-*g*-PAA2	8.0	1.63	42	6.939
PVA-*g*-PAA3	8.0	5.10	9	4.673

with different grafts length and average number N per molecule. The $\overline{M}_v$ values of graft chains were determined according to Reference [17]. The N values were calculated on the basis of the elemental analysis data [18], but considering the water content in graft copolymers. The molecular characteristics of graft copolymers are specified in Table 1. The same synthesis method was used to obtain PAA sample with $\overline{M}_v = 4400000$.

^{1}H NMR and proton-decoupled ^{13}C NMR spectra were recorded with a Varian Mercury-400 spectrometer operating at 400 MHz and 100 MHz correspondingly. The polymers were examined at room temperature with concentration varying from 0.001–0.1 g/cm^3. The only suitable solvent was D_2O, which serve as a lock signal. ^{1}H chemical shifts of graft copolymers were measured referencing to H_2O peak position on the ppm scale under the same conditions as PAA. Acetone at 30.2 ppm was used as reference for ^{13}C chemical shifts determination. The elucidation of PAA homopolymer microstructure in particular monomer links stereoregularity has been performed using literature data [19] where authors obtained good resolved ^{13}C NMR spectrum for low-molecular-weight PAA.

RESULTS AND DISCUSSION

Although ^{13}C NMR spectroscopy has been used extensively to study a stereoregularity in vinyl polymers [20] only a few works have been reported on polyacrylamide. Previously published spectra [20–22] have shown only a suggestion of splitting arising from different configurational sequences. Lancaster J. E. and O'Connor M. N. [19] found a significant improvement in resolution when low-molecular-weight PAA solutions were examined at elevated sample temperature. Their resulting spectrum showed the methylene, methine and carbonyl carbons of head-to-tail vinyl polymer. Figure 1(a) show the methine and methylene carbon regions. From the overall line shapes it is evident the similarity of described in literature (Fig. 1(a)) [19] and measured (Fig. 1(b)) methine and methylene fragments of spectra, which testifies to nigh stereochemical building of investigated polymers.

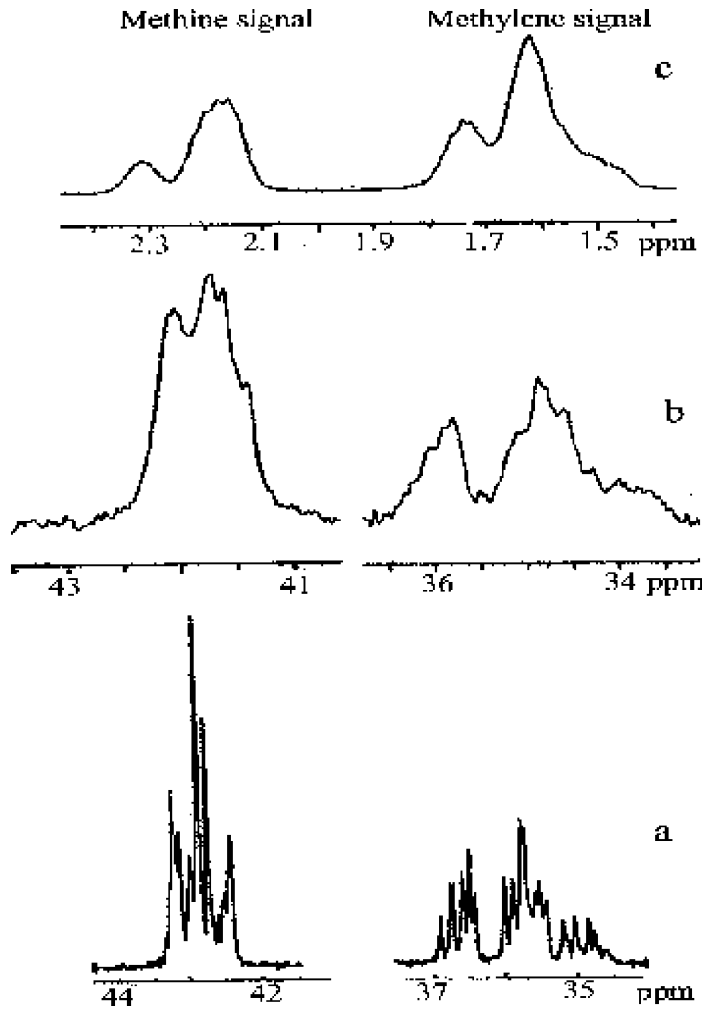

FIGURE 1 Literature [19] (a), experimental ^{13}C (b) (0.1 g/cm^3 solution in D_2O) and ^1H (c) (0.01 g/cm^3 solution in D_2O) methine and methylene resonances of polyacrylamide.

Bad resolution of experimental ^{13}C NMR spectrum of PAA can be explained with room temperature of NMR study and high molecular weight of examined PAA sample. High-molecular-weight sample show a well-resolved methine triplet but beyond molecular weigh $\cong 2 \times 10^6$ the line broadening becomes more severe [19]. Figure 1(c) shows the corresponding experimental ^1H NMR methine and methylene resonance of PAA.

The methine resonance (Fig. 1(a)) [19] is a triplet (triad sensitivity), which is father split showing pentad sensitivity. The low-field and high-field triplet peaks are assigned to the rr (syndiotactic) and mm (isotactic) sequences, respectively. This assignment is based on the slight intensity changes which authors of Reference [19] observed with sample prepared at lower temperature in which syndiotactic placements expected to be slightly favored. The central peak corresponds to heterotactic sequences (mr + rm). Using a *meso* placement probability of $P_m = 0.43$, estimated from mm/rr ratio (assuming Bernoulli statistics), the assignment to pentad sequences follows from the calculated intensities. Least certain is the identification of the rr-centered pentads, since further splitting due to heptad sensitivity distorts the line shapes in this region. The methylene carbon lines (Fig. 1(a)) fall into three fairy well-separated groups with almost all of the 20 lines required by hexad sensitivity resolved. One possible assignment of the CH_2 lines in terms of hexad sequences has been carried out and simulated methylene spectrum, which gives a close match to the experimental trace, has been obtained [19]. So polyacrylamide obeys Bernoulli statistics with $P_m = 0.43$, which is not unlike other vinyl polymers.

As we have not obtained the good resolved ^{13}C NMR spectrum for homopolymer, PVA-*g*-PAA copolymers were investigated by ^1H NMR spectroscopy. The whole ^1H NMR spectrum of PAA is presented on Figure 2.

From the downfield side, resonance lines assignable to residual acrylamide, H_2O, CH and CH_2 protons of polyacrylamide can be clearly observed. The same spectra were obtained for graft copolymers. No CH and CH_2 protons of poly(vinyl alcohol) [23] are detected due to low content (~2 weight%) of PVA in PVA-*g*-PAA. The low quantity of monomer acrylamide, which spectrum is shown on Figure 3 is seen indicating on not complete conversion.

The methine and methylene ^1H resonance of PAA-*grafted* for different copolymers together with resonance lines of PAA are presented on Figure 4.

From the overall line shapes and peak percentage contribution to intensity of methine and methylene ^1H signals in the limits of integrating errors it is evident that the results obtained for PAA hold for PAA-*grafted* in different PVA-*g*-PAA samples (Table 2).

Insignificant differences in peak positions are observed due to their measurements referencing to H_2O. So the microstructure of polymers formed at homopolymerization and matrix copolymerization processes are not differed. The possible explanation for this is the weak interaction through H-bonds of monomer and growing oligomers with matrix. In this case a matrix is capable to relatively strong bond to

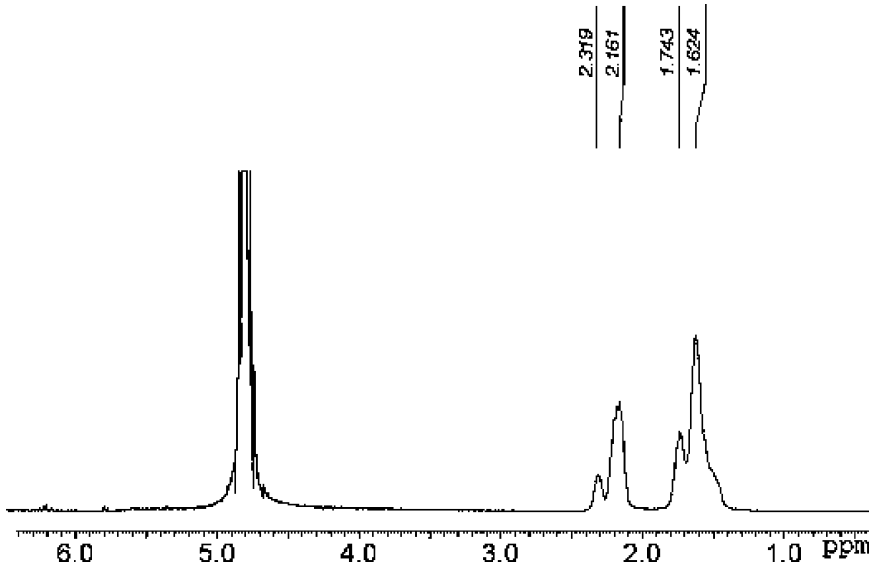

FIGURE 2 ^{1}H NMR spectrum of PAA (0.01 g/cm^3 solution in D_2O).

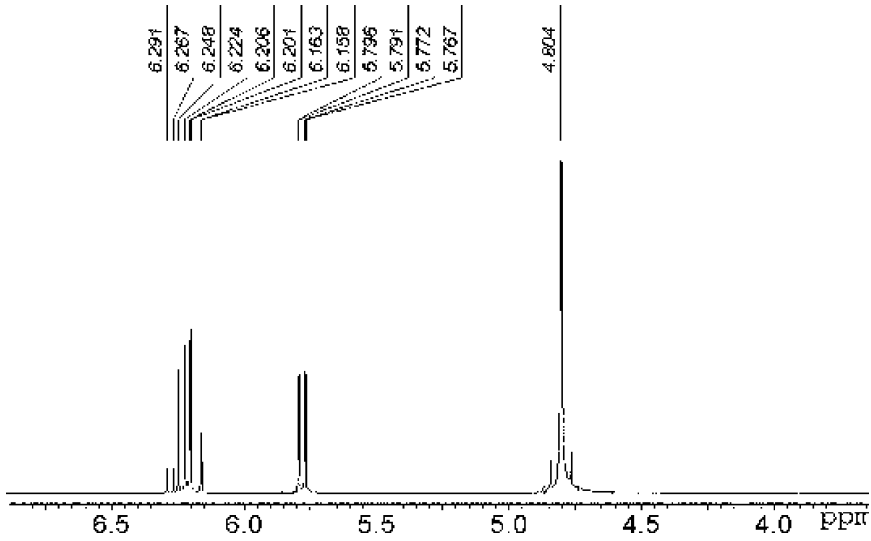

FIGURE 3 ^{1}H NMR spectrum of acrylamide (0.02 g/cm^3 solution in D_2O).

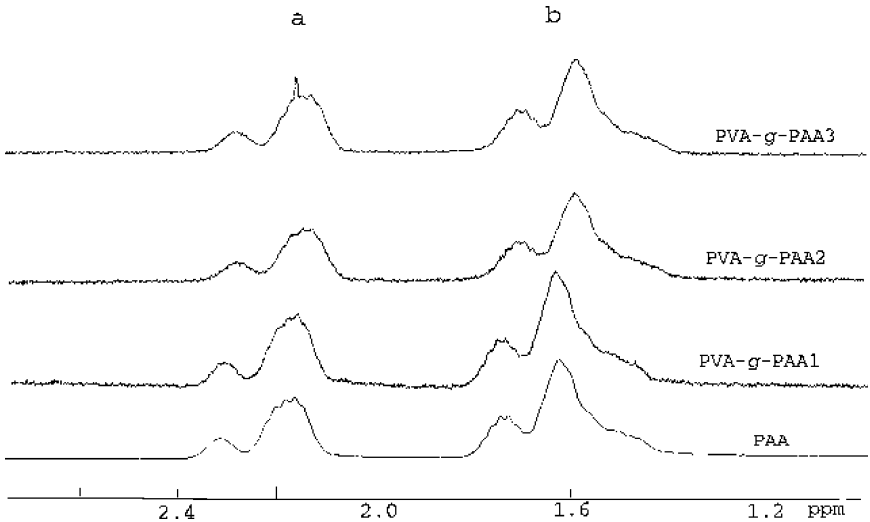

FIGURE 4 Methine (a) and methylene (b) ^{1}H resonances of PAA (0.01 g/cm^3 solution in D_2O) and PVA-*grafted* in different copolymers (0.001 g/cm^3 solution in D_2O).

complex the growing chain only after its length becomes more than some critical value. The "critical" length of growing chains is connected with PPC stability and depends on conditions of reaction passing. If only sufficiently long growing replica chain capable to recognize matrix the control is practically absent and structures formed at usual and matrix polymerization are not differed. So matrix graft copolymerization of PAA onto PVA backbone resulting in intramolecular PPC formation

TABLE 2 Peaks Position and their Percentage Contribution to Intensity of Methylene and Methine ^{1}H Signals for PAA and PAA-*grafted* in Different Copolymers

	δ, ppm				A, %			
Name	I[a]	II[a]	III[b]	IV[b]	I[a]	II[a]	III[b]	IV[b]
PAA	1,62	1,74	2,16	2,31	75,3	24,7	79,4	20,6
PVA-*g*-PAA1	1,62	1,73	2,16	2,31	74,5	25,5	73,9	26,1
PVA-*g*-PAA2	1,56	1,67	2,11	2,23	73,6	26,4	78,6	21,4
PVA-*g*-PAA3	1,53	1,65	2,07	2,22	73,7	26,3	79,0	21,0

[a]Methylene ^{1}H signals.
[b]Methine ^{1}H signals.

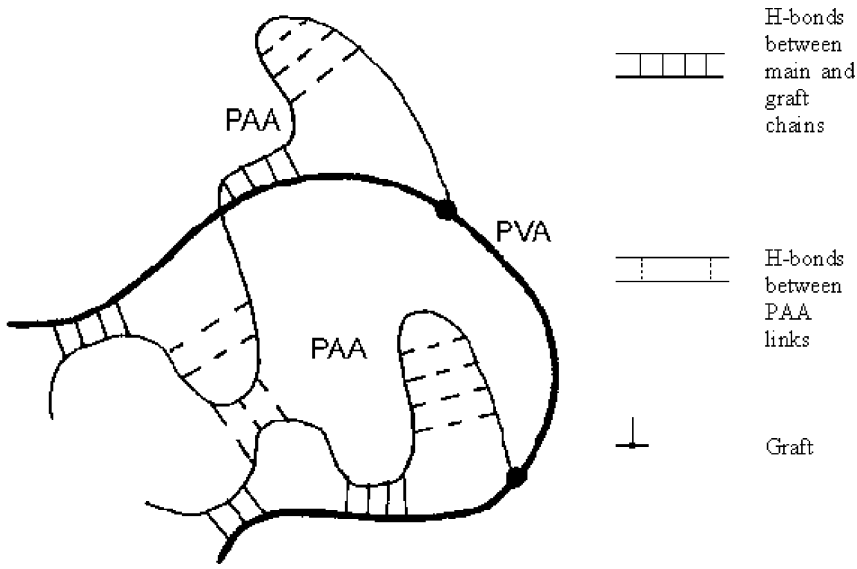

FIGURE 5 Schematic model for intramolecular polymer-polymer complex PVA-*g*-PAA.

where are a few contacts of replica chains with the main chain through H-bonding and sufficiently long unbound parts of replica chain (loops and tails) which interact between themselves (Fig. 5). This is supported by experimental results obtained previously by different methods [3–6].

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