

MICROSTRUCTURE OF PARTIALLY HYDROLYZED POLYVINYL ALCOHOLS USED IN PVC-S TECHNOLOGY

Radu N. OLARU¹, Dumitru Mircea VULUGA², Florentina GEORGESCU³,
Daniela MARINESCU⁴, Mihai DIMONIE⁵

Articolul prezintă un studiu comparativ al microstructurii unor alcooli polivinilici parțial hidrolizați folosiți în tehnologia PVC-S. Lungimea medie a secvențelor cu grupe acetat și distribuția lor în alcoolii polivinilici parțial hidrolizați, precum și „blocozitatea” lor au fost studiate pe baza spectrelor 1H-RMN ale alcoolilor polivinilici și a spectrelor UV ale complexilor alcool polivinilic-iod. S-a determinat o corelare lineară a blocozității (UV) cu indicele de blocozitate (RMN) pentru alcoolul polivinilic parțial hidrolizat în cataliza bazică.

The paper presents a comparative investigation on the microstructure of different partially hydrolysed polyvinyl alcohols used in PVC-S technology. Average acetate-containing sequence length and their distribution in partially hydrolyzed polyvinyl alcohols as well as their “blockiness” have been investigated via 1H-NMR of polyvinyl alcohols and UV spectra of polyvinyl alcohol-iodine complexes. For alkaline partially hydrolysed polyvinyl alcohols a linear correlation of blockiness (UV) with blockiness index (NMR) was found.

Keywords: polyvinyl alcohols, vinyl alcohol-vinyl acetate copolymers, sequence length, polyvinyl alcohol-iodine complexes UV spectra, polyvinyl alcohol ¹H-NMR spectra

1. Introduction

The suspension polymerization of vinyl chloride is a complex process and requires elaborate formulations. In the suspension polymerization of vinyl chloride the bulk monomer phase is dispersed in water by vigorous stirring and the droplets produced are stabilized against coalescence by the presence of suspending agents or protective colloids. The degree of protection afforded to the monomer droplets depends on the type, properties and concentration of the protective colloids [1-5]. Molecular composition and architecture of partially

¹ Engineer, S.C. Oltchim S.A., Ramnicu Valcea, Romania

² Senior Researcher, Centre for Organic Chemistry “C. D. Nenițescu” of the Romanian Academy, Bucharest, Romania, e-mail: vuluga@yahoo.com

³ Senior Researcher, S.C. Oltchim – Research Center, Ramnicu Valcea, Romania, e-mail: florentina_fg@yahoo.com

⁴ Chemist, S.C. Oltchim – Research Center, Ramnicu Valcea, Romania

⁵ Prof., Department of Macromolecules, University POLITEHNICA of Bucharest, Romania

hydrolyzed polyvinyl alcohols determine their properties as emulsifier and protective colloids. By combining information obtained from different chemical and spectral methods, a quantitative description of property and chemical composition of each polyvinyl alcohol is possible.

Many investigations involving the use of NMR spectroscopy in compositional studies of polyvinyl alcohols have been reported [6-10]. However, the data about the average sequence length and the intramolecular distribution of the co-monomers of various polyvinyl alcohols used in PVC-S technology are still not well documented.

In a previous paper [11] we presented the correlation of the degree of hydrolysis measured by the chemical method with the degree of hydrolysis determined from ^{13}C -NMR spectra. Moreover, we found that the carbonyl content determined from the infrared spectra, CO_{FTIR} , also correlate with the acetate content, AC_{NMR} , determined from ^{13}C -NMR spectra.

Here, we present the results of our investigation on the microstructure of some partially hydrolyzed polyvinyl alcohols used in PVC-S technology in terms of their degree of *blockiness* via UV and ^1H -NMR spectra.

2. Experimental

Different grades of water and alcohol soluble polyvinyl alcohols (PVA) have been used in this study. P1-P4, S1, and S2 are commercially available polyvinyl alcohols (Table 1). S3 and S4 are alcohol soluble polyvinyl alcohols samples obtained in laboratory by the alkaline alcoholysis of polyvinyl acetate in methanol, according to our method [11]. S5 is a solution of polyvinyl alcohol obtained in laboratory by the alcoholysis of polyvinyl acetate 50% wt in methanol, catalysed by sulfuric acid (2.5% wt) at reflux temperature (Table 1).

The degree of hydrolysis was determined by the saponification of a dried sample of polyvinyl alcohol followed by the titration, according to Japan Industrial Standard JTS K 6726-1977 [12].

Polyvinyl alcohols form intensely colored complexes when treated with an aqueous solution of iodine in potassium iodide in the presence of boric acid. This reaction has been used as a basis for an UV-VIS spectrophotometric method for the evaluation of the degree of *blockiness* (intramolecular distribution of the co-monomers) of the polyvinyl [13a-c]. The UV-VIS spectrum of each sample of polyvinyl alcohol-iodine complex, stabilized with boric acid, was recorded on a SPECORD 250-222A181 UV-VIS spectrometer (Analytic Jena, Germany), in 1 cm cell, on 0.2 g/L solutions of polyvinyl alcohols in water (P1-P4) or on 0.2 g/L solutions of polyvinyl alcohols in a mixture of methanol:water 1:1 v/v (S1-S5 samples). The absorption maxima of the complex formed by the each polyvinyl alcohol sample with iodine are shown in Table 1.

K Values of polyvinyl alcohols were determined from measurements of the relative viscosity of the polymer solutions and calculated according to Fikentscher's equation multiplied by 1000 [13c,14].

Molecular weight of polyvinyl alcohols have been measured in a mixture of water:methanol, 1:1 on Ultrahydrogel columns (exclusion limits 8×10^4 and 4×10^5 D, respectively), using a Size Exclusion Chromatograph Waters equipped with a refractive index detector. The mobile phase was a mixture of methanol:water, 1:1. Molecular weights were calculated against a calibration curve constructed using polyethylene glycol standards [11].

^1H -NMR spectra were recorded at 30°C on a VARIAN UNITY INOVA 400 instrument, at 400 MHz, with 3 sec recycle delay. Chemical shift (δ) was referenced to solvent peak (DMSO- d_6), at 2.5 ppm.

3. Results and discussion

Partially hydrolyzed polyvinyl alcohols are copolymers of vinyl acetate-vinyl alcohol. Determination of co-monomer sequences is important in the structural characterization of polyvinyl alcohols because *blockiness* is believed to affect many important properties such as melting points, surface activity, dispersing power, solubility and aqueous solutions viscosities.

The intramolecular distribution of residual acetate groups (degree of *blockiness*) in partially hydrolyzed polyvinyl alcohols was firstly estimated from the UV-VIS spectra of the polyvinyl alcohols-iodine complexes (Table 1).

Table 1

Polyvinyl alcohol (PVA) samples							
PVA	Degree of hydrolysis (% mole)	UV-VIS spectra of PVA-iodine complex		K value	Molecular weight (SEC)		
		Absorbance	λ (nm)		M_w	M_n	Polydisp.
P1 ^{a)}	84.51	0.4042	638.6	70	76124	42524	1.7901
P2 ^{b)}	74.03	0.5343	631.2	46	29266	13165	2.2230
P3 ^{c)}	80.12	0.5316	641.6	79	97706	53016	1.8429
P4 ^{d)}	87.52	0.3005	635.9	71	77892	40839	1.9072
S1 ^{e)}	56.43	0.4322	620.4	20	11723	3227	3.6326
S2 ^{f)}	47.80	0.2077	603.1	26	14376	4418	3.2540
S3 ^{g)}	51.05	0.2854	603.1	25.5	12071	3536	3.4139
S4 ^{g)}	57.92	0.350	618	25	13210	3728	3.5437
S5 ^{g)}	55.85	0.1574	585.8	24	13760	3989	3.4494

^{a)} Celvol E 26/88 (Celanese); ^{b)} Alcotex B72 (Harlow Chem. Comp. Ltd., UK); ^{c)} Gohsenol KH 17 (Nippon Gohsei, JP); ^{d)} Mowiol 26/88 (Kuraray, JP); ^{e)} Inovol SA5 (Ineos); ^{f)} Polivic S 202 (3V Sigma S.p.A.); ^{g)} sample prepared in laboratory

According to these data, the water soluble polyvinyl alcohol samples P2 and P3 have the highest degrees of *blockiness*. The alcohol-soluble polyvinyl alcohol sample S1, used as secondary suspending agent in PVC technology, is also a blocky sample. The alcohol-soluble polyvinyl alcohol sample S2, often used as secondary suspending agent in PVC technology, has a random-like distribution. All these data are in good correlation with the manufacturer's specification. According to these UV-VIS spectral data, an even clearer random distribution shows the alcohol-soluble polyvinyl alcohol sample S5, prepared in laboratory by the alcoholysis of polyvinyl acetate with methanol in the presence of the acid catalyst.

All ^1H -NMR spectra of partially hydrolyzed polyvinyl alcohols differ in relative intensities of the three resonance peaks in the hydroxyl protons region, in the number and intensities of resonance lines in the methylene and methine protons regions.

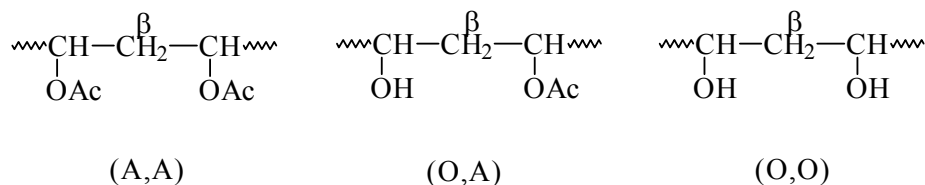
In ^1H -NMR spectra, the acetate substituted methine protons appear as three separate peaks between 4.77–5.10 ppm. These three peaks correspond to the compositional triads: acetate-acetate-acetate (A,A,A), hydroxyl-acetate-acetate (O,A,A) and hydroxyl-acetate-hydroxyl (O,A,O) from high to low fields. As the degree of hydrolysis of polyvinyl alcohols increases, the relative intensities of these peaks decrease. Between 3.38–3.88 ppm, the alcohol substituted methine protons appear as broad peaks.

Hydroxyl resonances appear as three separate peaks at about 4.26 ppm, 4.49 ppm and, respectively, at 4.67 ppm, attributed to (O,O,O), (A,O,O) and respectively, (A,O,A) compositional triads.

The methylene proton resonances, centered at about 1.40, 1.55 and 1.75 ppm are rather broad due to compositional and configurational splitting. These three peaks have been assigned to the three dyads: hydroxyl-hydroxyl (O,O), acetate-hydroxyl (A,O) and acetate-acetate (A,A) respectively.

The broad singlet centered at about 1.95 ppm represents the methyl protons in residual acetate groups.

Quantitative information about the microstructure of polyvinyl alcohols was easily obtained from the three methylene dyads. Mean sequence lengths of comonomers and the degree of *blockiness*, expressed as *blockiness* index (η), were estimated from the methylene resonances of vinyl alcohol and vinyl acetate residual groups in ^1H -NMR.



The integral ratios of methylene protons $H_\beta(\text{A,A})/\text{CH}_3$, $H_\beta(\text{A,O})/\text{CH}_3$ and $\text{CH}_\beta(\text{O,O})/\text{CH}_3$ were correlated to the quantitative ratios of acetate-acetate (A,A), acetate-hydroxyl (A,O) and hydroxyl-hydroxyl (O,O) dyads, respectively.

The calculation model was adapted from the previous research works [7,8,10], according to the following equations:

$$\text{Mole \% (OAc)} = 100 \cdot [2 \cdot I(\text{CH}_3) / 3 \cdot I(\text{CH}_2)]$$

where: $I(\text{CH}_3)$ represent the total peak intensities of the methyl proton resonances and $I(\text{CH})$ represent the total peak intensities of the methine proton resonances;

$$\text{Mole \% (OH)} = 100 - (\text{OAc})$$

$$\text{Mole\% (A,A)} = 100 \cdot [(A,A) / (A,A + A,O + O,O)]$$

$$\text{Mole\% (A,O)} = 100 \cdot [(A,O) / (A,A + A,O + O,O)]$$

$$\text{Mole\% (O,O)} = 100 \cdot [(O,O) / (A,A + A,O + O,O)]$$

Average sequence lengths of co-monomers and the *blockiness* index (η), were calculated from methylene dyads (O,O), (O,A) and (A,A) in $^1\text{H-NMR}$ recorded in water as follows:

$$L_{\text{OH}} = 2(\text{OH}) / (\text{O,A})$$

$$L_{\text{OAc}} = 2(\text{OAc}) / (\text{O,A})$$

$$\eta = (\text{O,A}) / 2[(\text{OH}) \cdot (\text{OAc})]$$

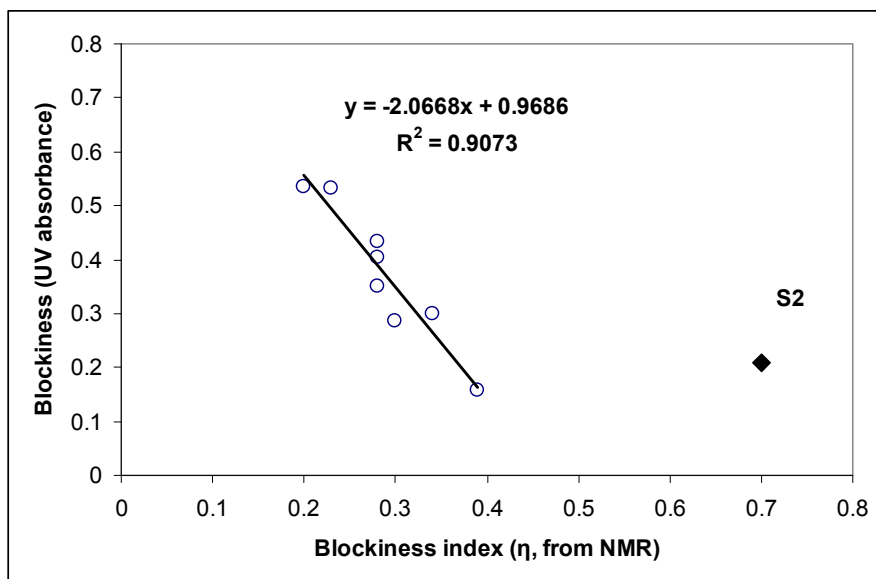
Blockiness index (η) is a convenient guide to characterize a sequence distribution in binary copolymers and it was defined [7,10] as a measure of deviation from the random character of these copolymers: $0 \leq \eta < 1$ is a characteristic value of block copolymers; $\eta = 1$ means completely random copolymers; $1 < \eta \leq 2$ indicate that co-monomers tend to alternate in the copolymer structure.

Table 2

Parameters derived from ^1H -NMR spectra

Sample	OAc (% mole)	OH (% mole)	Ratio (A,A)/CH ₃	Ratio (A,O)/CH ₃	Ratio (O,O)/CH ₃	L _{OH}	L _{OAc}	η
P1	11.73	88.27	0.512	0.329	4.84	30.52	4.06	0.28
P2	27.90	72.1	0.495	0.195	1.698	17.65	6.83	0.20
P3	21.90	78.10	0.472	0.241	2.325	20.29	4.93	0.23
P4	12.38	87.62	0.402	0.400	4.582	23.6	3.33	0.34
S1	44.68	55.32	0.548	0.211	0.732	7.80	6.30	0.28
S2	54.97	45.03	0.442	0.420	0.351	2.60	3.18	0.70
S3	48.78	51.22	0.562	0.204	0.60	6.85	6.52	0.30
S4	44.59	55.41	0.562	0.210	0.723	7.92	6.37	0.28
S5	47.80	52.20	0.450	0.270	0.674	5.38	4.93	0.39

The relative areas of these dyads should correspond to the *blockiness* of the sample. A large content of hydroxyl-hydroxyl (O,O) dyad corresponds to a longer mean run length of alcohol unit, revealing a blocky distribution. The (A,O) value decrease as the sequence distribution becomes blockier and should be 0 for di-block copolymers. Reversely, (A,O) value increases as the sequence distribution becomes alternate-like. A large content of acetate-hydroxyl (A,O) dyad reveal a random or alternating sequence distribution (Table 2).

Fig. 1 Blockiness correlation from UV and ^1H -NMR spectra

The *blockiness* of partially hydrolyzed polyvinyl alcohol samples determined from the absorbance in UV-VIS of polyvinyl alcohol-iodine complexes (Fig. 1) fairly correlate with the *blockiness* index, η , obtained from ^1H -NMR spectra. Surprisingly, the *blockiness* index, η , calculated from ^1H -NMR spectrum of S2 sample is much larger than we expected based on the absorbance determined from the UV-VIS spectrum of polyvinyl alcohol-iodine complex. This observation suggests that the absorbance in UV of polyvinyl alcohol-iodine complexes should be used for *blockiness* measurements for polyvinyl alcohols with at least 50% hydrolysis degree.

4. Conclusions

The characterization of some polyvinyl alcohols used in PVC-S technology was performed in terms of the degree of *blockiness* and *blockiness index* via UV-VIS and ^1H -NMR spectroscopy, respectively. The UV-VIS spectra of polyvinyl alcohol-iodine complexes, stabilized with boric acid, give a first and fair comparative view of the *blockiness* of different partially hydrolyzed polyvinyl alcohol samples. The average sequence lengths and the *blockiness index* were determined via ^1H -NMR spectra. The *blockiness* of water soluble and alcohol soluble polyvinyl alcohols determined from the absorbance in UV-VIS of polyvinyl alcohol-iodine complexes linearly correlate with the *blockiness index*, η , obtained from ^1H -NMR spectra.

REFERENCES

- [1]. A. K. Sanderson, Brit. Polym. J., **12** (1980) 186
- [2]. M. W. Allsopp, Pure Appl. Chem., **53** (1981) 449
- [3]. M. W. Allsopp, in "Manufacture and Processing of PVC", Applied Science Publ., London, 1982, chapter 7, p. 151
- [4]. M. Clark, in "Particulate Nature of PVC", Applied Science Publ., London, 1982, chapter 1, p. 15.
- [5]. S. Curcaneanu, S., M. Patrascu, P. Gluck, Rev. Chim. (Bucuresti), **35**, nr. 8, (1984) 718
- [6]. J. Shaefer, D. F. Natusch, Macromolecules, **5** (1972) 416-420
- [7]. T. Moritani, Y. Fujiwara, Macromolecules, **10** (1977) 532-535
- [8]. G. van der Velden, J. Beulen, Macromolecules, **15** (1982) 1071-1076.
- [9]. S. Toppet, P. J. Lemestra, G. van der Velden, Polymer, **24** (1983) 507- 512
- [10]. B. M. Budhlall, K. Landfester, D. Nagy, E. D., Sudol, V. L. Dimonie, D. Sagl, A. Klein, A., M. S. El-Aasser, Macromol. Symp., **15** (2000) 63-84.
- [11]. R. N. Olaru, M. Vuluga, F. Georgescu, D. Militaru, C. Draghici, M. Dimonie, Materiale Plastice, in press
- [12]. C. A. Finch, in "Polyvinyl Alcohol Developments", John Wiley & Sons, Chichester, ed. C.A. Finch, 1992, Appendix 1, p. 753-760

- [13]. a) *C. D. West*, J. Chem. Phys., **17**, 1949, p. 219; b) *J. H. Finley*, *Analyt. Chem.*, **33** (1961) 925; c) *C. A. Finch*, in "Polyvinyl Alcohol-Properties and Applications", 1st ed., John Wiley & Sons, Chichester, ed. Finch, C.A., 1973, Appendix 3, p. 561
- [14]. *D. E. Witenhafer*, in "Encyclopedia of PVC", 2nd ed., **1**, Marcel Dekker Inc., ed. Nass, L.L. & Heiberger, C.A., New York, 1985, p. 315.