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Stereochemical structure of polymer systems bearing a vitamin E substituent studied by ^{13}C n.m.r. spectroscopy

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The microstructural analysis of poly(α-tocopherylmethacrylate) (PMVE) was carried out by one-dimensional ^{13}C n.m.r. spectroscopy. The sensitivity of both aromatic and methyl (those attached to the aromatic ring) carbon signals to the stereosequences depends mainly on the proximity of these carbons to the maximum shielding zone of the neighbouring conjugated blocks formed by the aromatic ring and the pyran cycle. The sensitivity of the ester carbonyl signal to the chain microstructure is influenced mainly by the γ-gauche shielding effect. For PMVE prepared by radical polymerization Bernoullian statistics account satisfactorily for the observed relative intensities at the triad and pentad level. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Different derivatives of vitamin E are known for their antioxidant properties, which have been related to the preservation of cells[1] and can be used as an anti-aging agent. The polymeric system bearing vitamin E would be of interest as a bioresorbable polyagent. Although macromolecular compounds may display biological activity in their polymeric form, in general the biological activity is produced gradually as the pharmacological active agent is released by the selective biodegradation of the polymeric system[2–5]. If vitamin E molecules are linked to a methacrylic backbone through an aromatic ester bond of limited stability in the biological environment, it could be hydrolysed under mild conditions controlling the release of the active agent.

The ease of biodegradation of polymer systems in the living organism depends primarily on their chemical structure[6], but the enzymatic degradation of a given susceptible bond (i.e. an ester bond) is also affected by the stereochemical configuration of the polymer chains[7–9]. ^{13}C n.m.r. spectroscopy, due to its great sensitivity to structural detail, is the best method for investigating the microstructure of pharmacologically active polyacrylates[10–12]. In the present work we have investigated the polymeric system bearing vitamin E.

EXPERIMENTAL SECTION

Monomeric compound

α-Tocopherylmethacrylate (MVE) was prepared by the esterification of α-tocopherol (1.0 mol eq to 430.72 g) with excess of methacryloyl chloride (4.0 mol eq to 418.4 g) in the presence of triethylamine and diethylether as solvent. The reaction mixture was allowed to stand under nitrogen until esterification was complete. The chlorhydrate of triethylamine was filtered off and the methacrylate derivative of vitamin E (MVE) was concentrated at reduced pressure. *Scheme 1* shows the structure of this monomer. The yield was 70%.

Polymer

Poly(α-tocopherylmethacrylate) (PMVE) was prepared by polymerizing the monomer MVE at 50°C in a solution of DMF ([MVE] = 1 mol l^{-1}), using 2,2-azobisisobutyronitrile (AIBN) as free radical initiator. The reaction was carried out in Pyrex glass ampoules sealed under high vacuum. After polymerization for 5 h the reaction mixture was poured into a large excess of methanol and the precipitated polymer was washed with methanol and dried under reduced pressure to constant weight.

n.m.r. measurements

^{13}C n.m.r. spectra were recorded on a Varian XL-300 spectrometer (operating at 75 MHz for ^{13}C n.m.r.) at 30°C using 10% (w/v) solutions in $CDCl_3$ with hexamethyldisiloxane as internal reference. The areas under the n.m.r. signals were determined by the method of cutting and weighing, as well as from integrated intensities. Overlapping peaks were resolved by deconvolution.

Theoretical calculations

Semi-empirical calculations were carried out using the original parameters of the program AM1[13], based on the restricted Hartree–Fock (RHF) method, included in MOPAC version 6.0[14]. The program ran on an ALPHA 2100 computer at the Computer Centre of CSIC (Madrid, Spain). Further calculations were carried out using the program Insight II running on a Silicon Graphics Indigo-2 workstation.

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Initial geometries were obtained by molecular mechanics (MM +) by means of the program Hyperchem version 4.5[15]; this program ran on a Silicon Graphics Indigo-2 workstation. The results of this optimization were used as input data for the semi-empirical calculations. The same program was used to visualize the structures obtained after MOPAC minimization. Geometries were optimized in internal coordinates. The optimization was stopped when Herbert or Peter tests were satisfied in the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method[16]. The PRECISE option was applied during the optimization process with the gradient norm set to 0.01. The calculations were carried out with full geometry optimization (bond lengths, bond angles and dihedral angles).

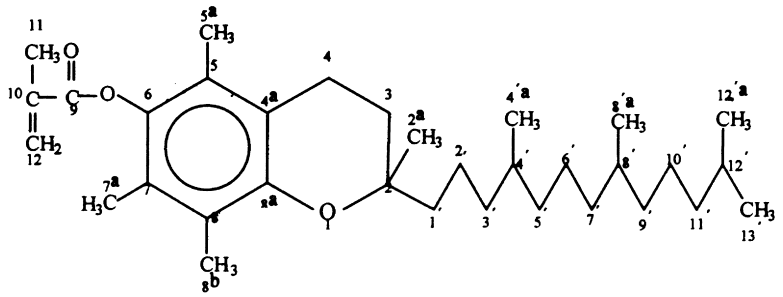
Mulliken population analyses[17] used to discuss the electron distributions are adequate for present purposes because they reflect the trend in populations and charges which appear to be important rather than their actual values.

RESULTS AND DISCUSSION

The monomer MVE spectra

The ^{13}C n.m.r. spectrum of MVE is shown in *Figure 1*. The assignment of the signals (*Figure 1* and *Scheme 1*) was made according to the following criteria:

(1) (i) Spectra of the model compounds having pyran and methacrylate residues[18]
(2) (ii) Data, presented by Matsuo[19], for the carbon spectrum of α-tocopherol
(3) (iii) Multiplicity of the carbon signals as revealed in the spectra recorded with application of the DEPT sequence[20]
(4) (iv) Additive scheme calculation of the aromatic carbon chemical shifts[21] on the basis of the spectrum of α-tocopherol[18] using the difference in the values of substituent increments for OH and for OC(O)C $(CH_3)=CH_2$[18]



Scheme 1 Structural formula of the monomer α-tocopherylmethacrylate (MVE). Designation of the carbons as in the spectrum presented in *Figure 1*

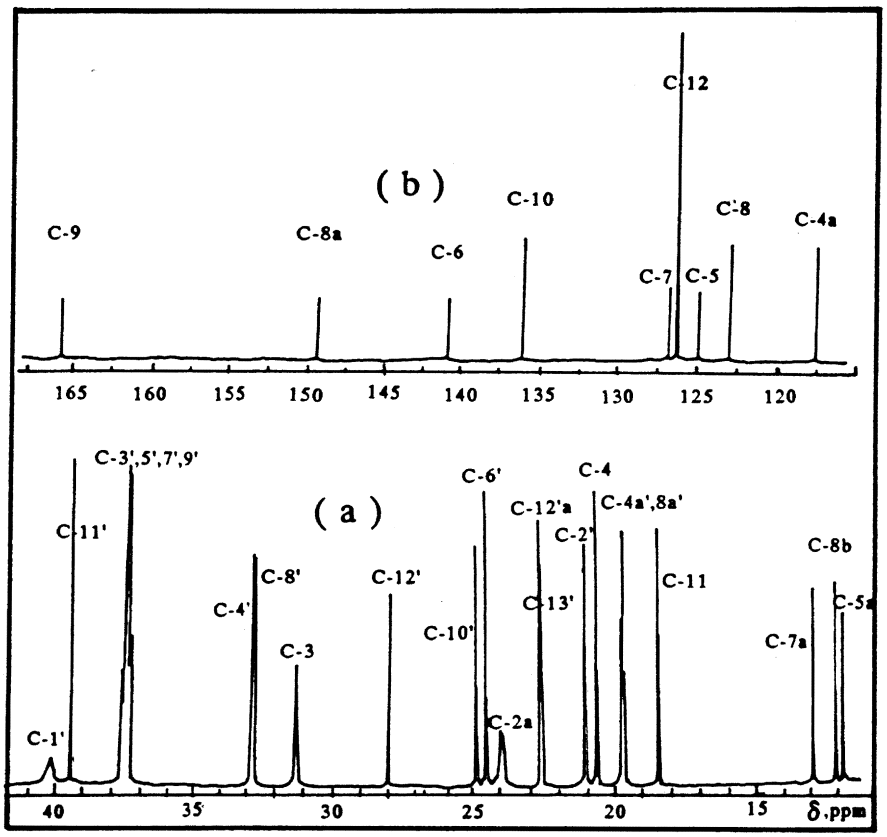


Figure 1 ^{13}C NMR spectra (75 MHz) of α-tocopheryl methacrylate (MVE) recorded in $CDCl_3$ at 30°C: the alkyl and heterocyclic carbon region (a); the carbonyl, olefinic and aromatic carbon region (b). The carbon signal designation in accordance with *Scheme 1*

(5) (v) Additive scheme calculation for branched alkanes using a linear equation suggested by Grant and Paul[22].

The splitting of the signals from Me-groups linked to the alkyl chain (CH_3-8′a, CH_3-4′a) into two peaks arises from the configuration isomerism of this chain, while the observed splitting of cyclic carbon signals (C-3 and C-2) and those of the carbons attached to the cycle (C-2a and C-1′) reflects the isomerism of the disubstituted cycle – axial or equatorial disposition of the methyl and branched alkyl substituents and their α-effect at the cycle carbons[20]. End methyl groups C-12′a and C-13′a are observed to be non-equivalent due to their diastereotropic character.

The assignment of the Me-groups attached to the aromatic ring (CH_3-7a, CH_3-8b and CH_3-5a) appears to be important for the further analysis of the carbon spectrum of PMVE. Signals from CH_3-5a and CH_3-7a were distinguished from CH_3-8b by taking into account that the substitution of the OH for $C(O)C(CH_3)=CH_2$ group should induce more effect ($\Delta\delta$) at the chemical shifts of CH_3-7a and CH_3-5a disposed closer to the substitution site than CH_3-8b. The assignment presented in *Figure 1* (according to which values of $\Delta\delta$ for CH_3-7a, CH_3-5a and CH_3-8b are 0.77, 0.56 and 0.22 ppm, respectively) is consistent with this assumption.

The polymer (PMVE) spectra

Region of the methyl carbon attached to the phenyl ring. Expanded-CH_3 signals of the 75 MHz ^{13}C spectrum of PMVE are presented in *Figure 2*. The assignment of the methyl carbon signals (designation in accordance with *Scheme 1*) was made on the basis of the monomer spectrum (*Figure 1*a) according to which the chemical shifts of the CH_3-group signals increase in the order: **CH_3-5a** < **CH_3-8b** < **CH_3-7a**. In this spectrum one can observe that all methyl carbon signals proved to be microstructure sensitive. This trend is attributed to the influence of the neighbouring side-chain substituents[23]. The γ-gauche effect can be excluded from the consideration because only the aromatic carbons of the rigid phenyl ring[23] are disposed in the γ-position to these CH_3-groups.

Thus, the CH_3-carbon signals appear to be affected by the polymer stereoregularity in spite of the fact that the influence of the side groups is reduced in the sterically crowded PMVE, due to the expansion of the backbone valence angle $\angle C{-}CH_2{-}C$ some 15° from the normal tetrahedral value[24]. This geometric feature was calculated by molecular modelling using the molecular mechanic methods MM+ and CVFF, a force field of Biosym which has been used to accurately model geometric parameters of conjugated systems. The models used are shown in *Figure 3*. Model A is a monomeric unit of PMVE end-capped by methyl groups. Model B has 3 monomeric units of PMVE also end-capped by methyl groups and model C is a trimeric molecule similar to B where the methacrylate backbone has been replaced by an acrylate backbone. Model A was used to check whether there were geometric changes in the aromatic rings and/or the pyran cycle relative to models B and C. The first conclusion is that there are no significant changes in the geometric parameters of the side group, and hence to the electronic properties of these models. The values obtained for the backbone valence angle $\angle C{-}CH_2{-}C$ in model B was 127.5° as calculated by MM+ and 127° using the CVFF force field. For model C (acrylate) the values were respectively 118° and 117.5°. Thus, the observed expansion of the backbone valence angle $\angle C{-}CH_2{-}C$ for several methacrylates with different substituents can be generalized for PMVE, and it may be explained by the steric effect of the methyl groups (*Figure 3*). In accordance with the molecular model of the monomer unit, the splitting of the ^{13}C aromatic carbon signals may be rationalized in terms of the conjugated system, formed by the aromatic ring and the oxygen of the pyran cycle directly attached to the phenyl group. The electronic parameters of model A were studied by the

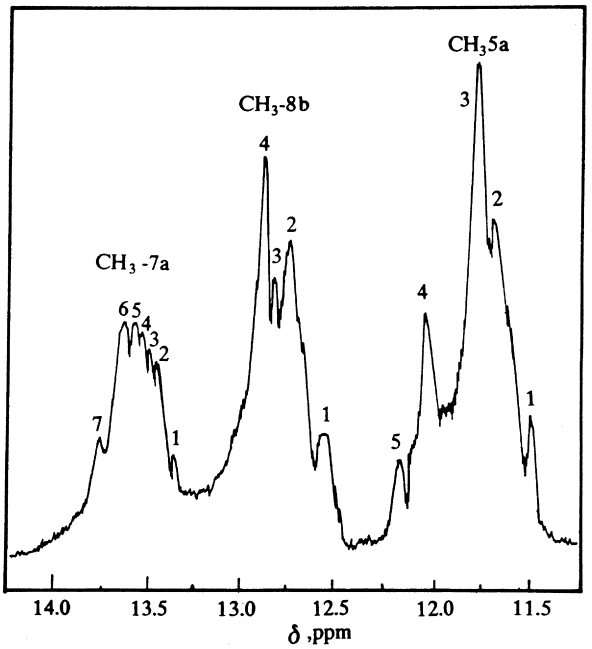


Figure 2 ^{13}C NMR spectrum (75 MHz) of PMVE (region of the methyl groups attached to the phenyl ring) recorded in $CDCl_3$ at 30°C. The carbon signal designation in accordance with *Scheme 1*

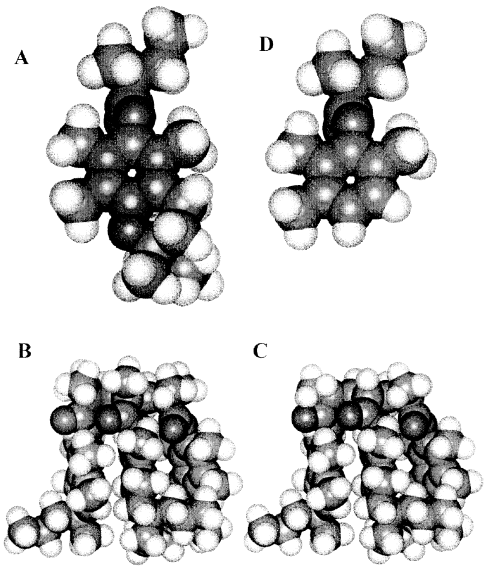
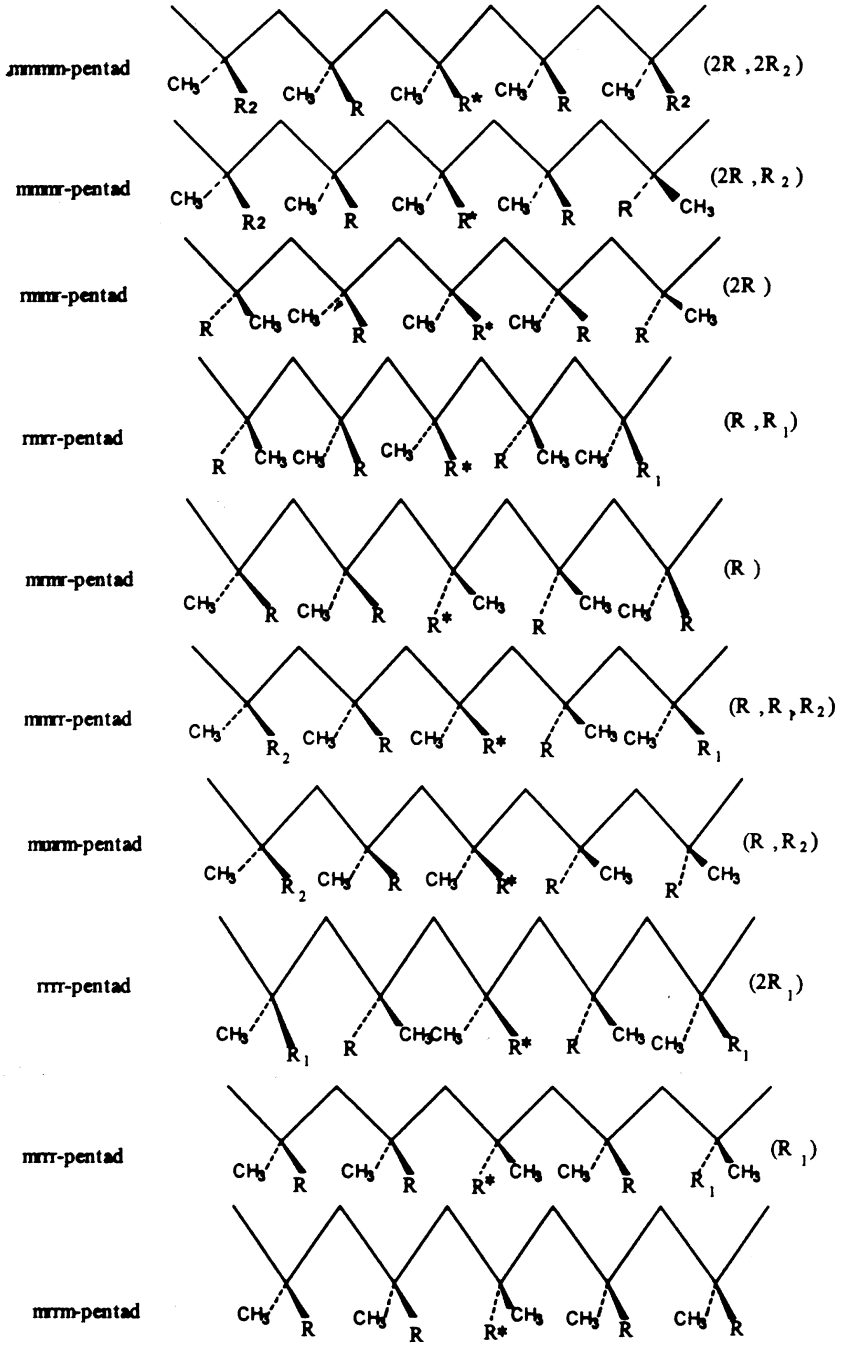


Figure 3 Molecular model of the monomer unit built up by means of the computer program Hyper Chem 40. The dihedral angles between aromatic ring plane and cycle atoms **C-1**, **C-4**, **C-3** and **C-7** are 178.3°, 179.07°, 171.9° and 172.5°, respectively. A, methyl end-capped model of the monomeric repeating unit of PMVE; B, the triad sequence model of the acrylate derivative of vitamin E; C, triad sequence of PMVE; D, methyl end-capped model of the monomeric repeating unit without the pyran side residue

semi-empirical quantum mechanics method AM1 in comparison with the model without the pyran group (model D). Model A has a Mulliken electronic density excess of 0.3541 ue and a π electronic density excess of 0.3086 ue. On the other hand, compound D has a Mulliken electronic density excess of 0.3772 ue and a π electronic density excess of 0.3463 ue. Therefore, the aromatic ring has a larger electronic density and it will strongly interact with the neighbouring rings. Taking this into account we can assume the neighbouring conjugated blocks to produce a considerable effect at the Me-groups of the central unit in triad and pentad (**CH**$_3$*) due to the high electronic density of these aromatic systems.

In the spectrum presented in *Figure 2* all methyl signals provide the information on the polymer chain at the pentad level: signal **CH$_3$-7a** is observed in an interval of $\Delta\delta = 0.46$ ppm (13.30–13.76 ppm) and splits into seven peaks; signal **CH$_3$-8b** is observed in an interval of $\Delta\delta = 0.37$ ppm (12.57–12.94 ppm) and splits into four peaks; signal **CH$_3$-5a** is observed in an interval of $\Delta\delta = 0.7$ ppm (11.50–12.20 ppm) and splits into five peaks.

In pentad sequences methyl carbons of the central unit (**R***) are influenced both by the first neighbour groups (**R**α) and by the second neighbour groups in the terminal dyads of the pentad structure ($\mathbf{R}_1^{\beta}, \mathbf{R}_2^{\beta}$) which have the same configurational arrangement as **R*** (see *Scheme 2*). The **CH$_3$-5a** signal appears to exhibit the greatest chemical shift dispersion among the various sequences. The low field component of this signal at 12.20 ppm we can tentatively assign to the m**rr**m pentad, keeping in mind that in this pentad neighbouring conjugated blocks producing the shielding (by analogy with the ring currents from the



Scheme 2 Pentad sequence in all trans planar zigzag conformations

aromatic ring[23]) effect ($\mathbf{R}^{\alpha}$ and $\mathbf{R}_1^{\beta}$) are remote from the $\mathbf{CH}_3$* (*Scheme 2*). The high field component at 11.50 ppm can probably be ascribed to the **mm** triad in which the chemical shift of the CH_3* appears to be insensitive to the stereochemical configuration of the monomeric unit on each end of this sequence (i.e. to the pentad structure) due to the weak effect produced by $\mathbf{R}_2^{\beta}$ in **mm**-centred pentads (*Scheme 2*). Such a conclusion seems to attribute to the fact that **mm**-centred pentads can be assumed to be more sterically constrained than **mr** and **rr** pentads and therefore appear to attain such conformations when bulky neighbouring groups are remote from each other and as a consequence

Table 1 Assignment of the ^{13}C NMR resonance signals of the methyl carbons attached to the phenyl ring for pentad sequences in the polymer chain of PMVE

Methyl carbon	Peak number	Integration limits in ^{13}C NMR, δ (ppm)	Sequence	Molar percentage	
				Experimental	Calculated[a]
CH_3-5a	1	11.45–11.52	**mm**	7	7
	2	11.52–11.70	r**mr**r	22	21
			m**rm**r		9
	3	11.70–11.90	m**mr**r	45	9
			m**mr**m		3
			r**rr**r		26
	4	11.92–12.14	r**rr**m	22	21
	5	12.04–12.25	m**rr**m	45	45
CH_3-7a	1	13.30–13.40	**mm**	7	7
	2	13.40–13.45	r**mr**r	19	21
	3	13.45–13.50	m**rm**r	11	9
	4	13.50–13.56	m**mr**r	12	9
			m**mr**m		3
	5	13.56–13.65	r**rr**r	24	26
	6	13.65–13.77	m**rr**r	23	21
	7	13.77–13.85	m**rr**m	4	45
CH_3-8b	1	12.43–12.59	**mm**	9	7
	2	12.59–12.76	r**mr**r	30	21
			m**rm**r		9
	3	12.76–12.83	m**mr**r	11	9
			m**mr**m		3
	4	12.83–13.10	**rr**	49	51

[a] According to Bernoullian statistics ($P_m = 0.29$; $P_r = 0.71$)

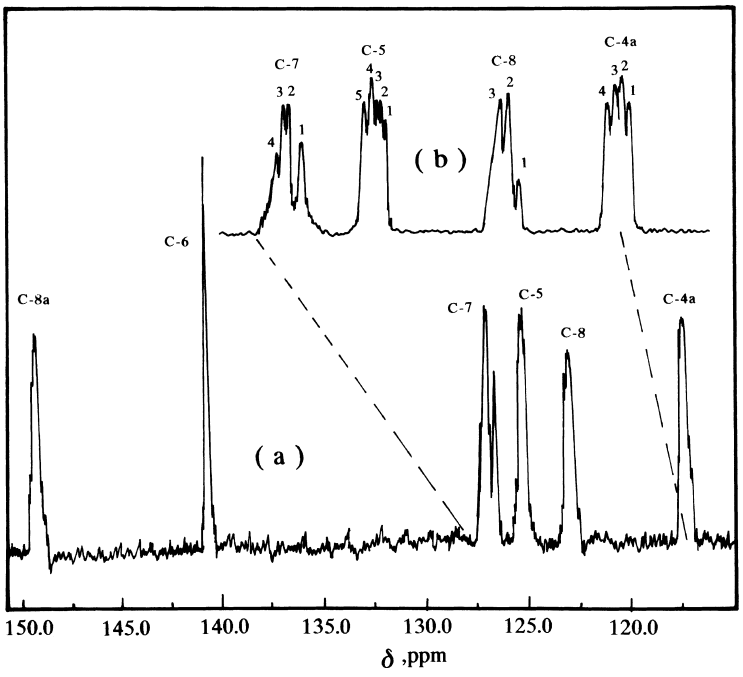


Figure 4 ^{13}C NMR spectra (75 MHz) of PMVE recorded in $CDCl_3$ at 30°C; the complete aromatic carbon region (a), the expanded region showing only signals sensitive to the polymer stereoregularity (b). The carbon signal designation in accordance with *Scheme 1*

their influence on the $\mathbf{CH}_3$* is reduced. The Bernoullian probabilities P_m and P_r (0.29 and 0.71, respectively) were obtained from the experimental estimates (using relative signal intensities of the corresponding peaks) of the **mm** and m**rr**m populations. It is noteworthy that these values are close to those determined for other methacrylates with a bulky alcohol residue (**A**) obtained by radical polymerization ($P_m = 0.26$ and $P_r = 0.74$ when $\mathbf{A} = OC_6H_4N{=}NC_6H_5$[25], $OC_6H_4NHC(O)CH_3$[26]).

The complete signal assignment was made (*Table 1*) on the basis of *Scheme 2* (keeping in mind that by the analogy with the ring currents from the aromatic ring[18] $\mathbf{R}^{\alpha}$ and $\mathbf{R}_1^{\beta}$ are assumed to produce the shielding while $\mathbf{R}_2^{\beta}$ produce the deshielding effect at the $\mathbf{CH}_3$*) and by a comparison of the experimental signal intensities with calculated pentad populations assuming Bernoullian trial[27].

Aromatic carbon region

The 75 MHz ^{13}C n.m.r. spectrum of PMVE is presented in *Figure 4*a. The assignment of the aromatic signals (designation in accordance with *Scheme 1*) was carried out on the basis of the monomer spectrum (*Figure 1b*). In this spectrum one can observe that signals of four aromatic carbons appear to be affected by the polymer stereoregularity. The expanded spectrum of these carbons (**C-7**, **C-5**, **C-8** and **C-4a**) is shown in *Figure 4*b. This observation can also be rationalized (as for the methyl carbon signals) in terms of the effect produced by the neighbouring conjugated ''blocks'' at the aromatic carbons of the central unit ($\mathbf{C}_{arom}$*) The γ-gauche shielding effect can be excluded from the consideration because only aromatic carbons being part of the rigid phenyl ring are γ to **C-7**, **C-5**, **C-8** and **C-4a**. The unique carbon that could be affected by the long-range γ-gauche interactions[28] is **C-6** but it does not exhibit any splitting. It is known that the chemical shifts of ^{13}C nuclei in aromatic compounds (relative to the ^{13}C benzene chemical shifts) are proportional to the excess of π electronic density or total electron density on the carbon.

Therefore, the electronic parameters of an aromatic compound can be used as a probe to assign the ^{13}C spectra of this kind of compound. We tried to obtain the assignment of the aromatic carbons of PMVE by means of the semi-empirical quantum mechanics method AM1. This method has been thoroughly checked to give a reasonable electronic density distribution on substituted benzenes. We should point out that the ^{13}C n.m.r. aromatic signals of MVE and PMVE are practically the same. Therefore, MVE can be used as the model. Moreover, for the sake of simplicity, we used the model A shown in *Figure 3*, where the monomer is end-capped with methyl groups and the aliphatic chain of the pyran group is a propyl group. The plot of ^{13}C chemical shifts of A versus the Mulliken charge is shown in *Figure 5*; it can be seen that there is a very good linear correlation. Furthermore, the observed correlation agrees with the assignment suggested above. The ^{13}C chemical shift assignment of carbons 5 and 7 is problematic because of their very close electronic density values.

In the spectrum presented in *Figure 4b* aromatic carbon signals provide the information upon the polymer chain microstructure at the pentad level; signal **C-7** is observed in an interval of $\Delta\delta = 0.55$ ppm (126.60–127.15 ppm) and splits into four peaks; signal **C-5** in an interval of $\Delta\delta = 0.39$ ppm (125.12–125.51 ppm) and splits into five peaks; signal **C-8** in an interval of $\Delta\delta = 0.40$ ppm (122.57–122.97 ppm) and splits into three peaks; signal **C-4a** in an interval of $\Delta\delta = 0.46$ ppm (117.21–117.67 ppm) and splits into four peaks. The complete assignment (*Table 2*) was made using the same criteria applied to assignment in the methyl carbon region.

The data enabling us to carry out the comparative analysis of the sensitivity of different methyl and aromatic carbon signals to sequences in the spectrum of PMVE are collected in *Table 3*. The shielding effect produced by the neighbouring conjugated ''blocks'' can be tentatively assumed to depend on both the spatial vicinity of the carbon of the central unit to the shielding zone[29] and the

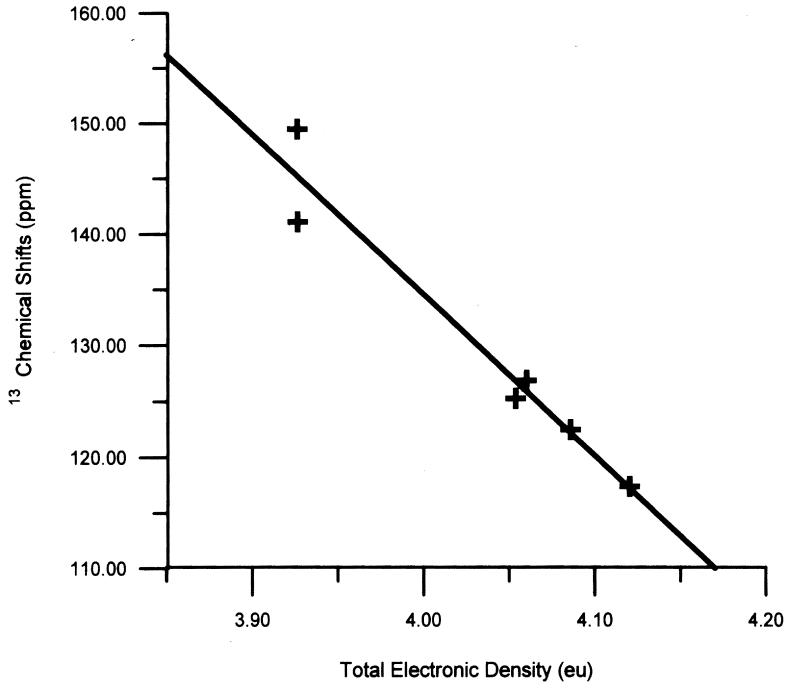


Figure 5 Variation of the ^{13}C NMR chemical shift of aromatic carbons as a function of the total electronic density calculated by semi-empirical methods according to the models drawn in *Figure 3*

Table 2 Assignment of the ^{13}C NMR resonance signals of the aromatic carbons for pentad sequences in the polymer chain of PMVE

Aromatic carbon	Peak number	Integration limits in ^{13}C NMR, δ (ppm)	Sequence	Molar percentage	
				Experimental	Calculated[a]
C-7	1	126.45–126.90	**mm**	30	8
			r**mr**r		21
	2		m**rm**r		9
		126.90–127.05	m**mr**r	23	9
			m**mr**m		3
	3	127.05–127.17	r**rr**r	24	26
	4	127.17–127.38	m**rr**r	23	21
			m**rr**m		4
C-5	1	125.0–125.05	**mm**	30	8
	2	125.05–125.25	r**mr**r		21
			m**rm**r		9
	3	125.25–125.32	m**mr**r	21	9
			m**mr**m		3
	4	125.32–125.47	r**rr**r	27	26
	5	125.47–125.68	m**rr**r	22	21
					4
C-8	1	122.41–122.57	**mm**	9	8
	2		r**mr**r		21
		122.57–122.81	m**rm**r	40	9
			m**mr**r		9
			m**mr**m		3
	3	122.81–123.04	**rr**	51	50
C-4a	1	117.0–117.15	**mm**	10	8
	2	117.15–117.27	r**mr**r	20	21
	3		m**rm**r		9
		117.27–117.52	m**mr**r	46	9
			m**mr**m		3
			r**rr**r		26
	4	117.52–117.75	m**rr**r	24	21
			m**rr**m		4

[a] According to Bernoullian statistics ($P_m = 0.29$; $P_r = 0.71$)

Table 3 Comparative analysis of the methyl and aromatic carbon signal sensitivity to the stereosequences in the polymer chain of PMVE

Carbon[a]	Total electronic density (eu)[b]	Overall spread of carbon chemical shift, $\Delta\delta$ (ppm)[c]	Value of $\boldsymbol{R}_1^{\beta}$ shielding effect[d]
CH_3-5a	4.171	70	14
CH_3-7a	4.196	46	8
CH_3-8b	4.171	37	0
C_{arom}-4a	4.120	46	11
C_{arom}-8	4.086	40	0
C_{arom}-5	4.054	39	9
C_{arom}-7	4.060	55	9
C_{arom}-6	3.927	0	0
C_{arom}-8a	3.926	20	0

[a] Carbon designation in accordance with *Scheme 1*
[b] Mulliken electron densities calculated by MOPAC version 6.0[14]
[c] In the spectrum presented in *Figures 2* and *4*
[d] Determined using chemical shifts of the **rr**-centred pentads

carbon electron density whose decrease seems to result in an increase of the carbon sensitivity to the shielding[21]. Methyl carbons having close electron densities exhibit different sensitivities; overall spread of chemical shifts and value of $\mathbf{R}_1^{\beta}$ – effect decrease in the order: **CH_3-5a** > **CH_3-7a** > **CH_3-8b**. This observation can be rationalized in terms of the steric constraint: **CH_3-7a** and **CH_3-8b** are ortho to each other and **CH_3-8b** is besides disposed closer than **CH_3-7a** to the chiral centre of the cycle bearing two bulky substituents. The steric factor seems to be prevalent hindering to more extent (in comparison with **CH_3-5a**) the extension of **CH_3-7a*** and **CH_3-5a*** to the maximum shielding zone of the neighbouring conjugated groups and (or) 'blocking' their influence. The order of the aromatic carbon electron

density decrease does not correlate with the order of the carbon sensitivity increase: so carbons **C-6** and **C-8** having the lowest electron density appears to be practically insensitive to the polymer chain microstructure. This trend can also be interpreted in terms of the steric hindrance: in the case of **C-6** – due to two Me- groups in ortho-position to it; in the case of **C-8a** – due to its vicinity to the chiral centre of the cycle (*Figure 3*). It is noteworthy that by taking into account the difference in the electron density the sensitivity to the chain microstructure observed for the aromatic carbons **C-5***, **C-7*** and **C-8*** appears to be less in comparison with that one exhibited by the methyl groups attached to the corresponding aromatic carbons **CH$_3$-5a***, **CH$_3$-7a*** and **CH$_3$-8b***, respectively (*Table 3*). This is probably due to the fact that methyl groups constrain the extension of the aromatic carbons into the maximum shielding zone of the neighbouring conjugated groups and (or) block their influence.

Carbonyl carbon region

In the 75 MHz ^{13}C n.m.r. spectrum of PMVE carbonyl signal is observed in an interval of $\Delta\delta = 0.9$ ppm (174.54–175.63 ppm) and splits into five peaks due to the pentad sequence; heptad effects are also detectable in the region of pentads m**rm**r and r**rr**r (*Figure 5*).

The observed splitting can arise from the γ-gauche shielding effect but the γ-gauche effect method cannot be successfully applied to the prediction of this stereo-sequence-dependent carbonyl carbon spectrum due to the conformational dependence of the PMVE backbone geometry[24]. In such a sterically crowded disubstituted vinyl polymer as PMVE the backbone valence angle at the quaternary carbon is suggested to depend on the conformations of the attached backbone bonds with $\angle CH_2{-}C{-}CH_2 = 106$, 111 and 116° when both attached backbone bonds are trans, when one is trans and the other is gauche and when both are gauche, respectively[19]. Variation of 10° in the $CH_2{-}C{-}CH_2$ valence angle might be expected to have a significant influence upon the dihedral angle (calculated by the six state RIS model[24]) between carbonyl and its γ-substituent quaternary carbon, producing a shielding effect and thus to result in the disparity between chemical shifts estimated via the γ-gauche effect method and the observed ones. The observed splitting of the carbonyl carbon signal can also be attributed to the influence of the neighbouring groups but only marginally in comparison with the γ-effect, all the more that in such sterically crowded polymer as PMVE the influence of the side groups is generally reduced due to the expansion of the backbone valence angle $\angle C{-}CH_2{-}C$ some 15° from the normal tetrahedral value[24].

The assignment of the ester carbonyl signals in the spectrum presented in *Figure 6* was made (*Table 4*) on the basis of the following criteria:

(1) (i) Comparative analysis of the assignment of pentad signals of the ester carbonyl carbon in the spectra of(meth)acrylates having different alcohol residue **A**[25–31] which shows that increasing size of the **A** results in the decrease of the observed chemical shift dispersion among the various **mm**-centred pentads (with 0.5, 0.09 and 0.0 ppm when **A** = OCH_3, $OC_6H_4NHC(O)CH_3$ and $OC_6H_4N{=}NC_6H_5$, respectively).

(2) (ii) Comparison of the experimental signal intensities with calculated triad and pentad population assuming Bernoullian statistics.

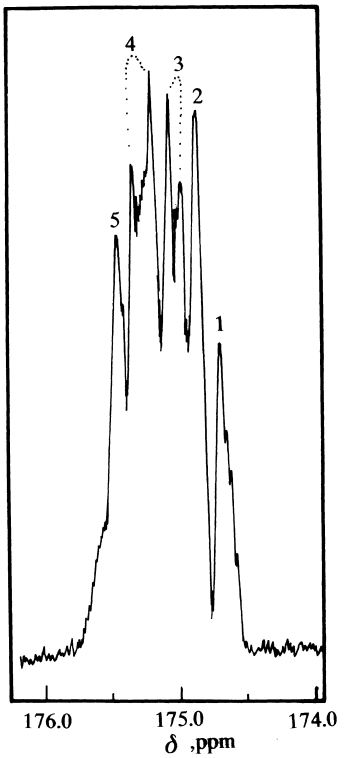


Figure 6 Expanded resonance signals of the carbonyl ester group of PMVE chains showing the influence of the stereoregularity of monomer sequences

Table 4 Assignment of the ^{13}C NMR resonance signals of the ester carbonyl carbon for pentad sequences in the polymer chain of PMVE

Peak number	Integration limits in ^{13}C NMR, δ (ppm)	Sequence	Molar percentage	
			Experimental	Calculated[a]
1	174.56–174.76	**mm**	11	8
2	174.76–174.93	r**mr**r	18	21
3	174.93–175.13	m**rm**r	19	9
		m**mr**r		9
4	175.13–175.44	m**mr**m	30	3
		r**rr**r		26
5	175.44–175.58	m**rr**r	22	21
		m**rr**m		4

[a] According to Bernoullian statistics ($P_m = 0.29$; $P_r = 0.71$)

The data collected in *Tables 1*, *2*, and *4* clearly show that for PMVE prepared by radical polymerization Bernoullian statistics provides a fit to the observed intensities at the triad and pentad level. This conclusion is consistent with results obtained for other methacrylates with a bulky alcohol residue[24,26–28]. The analysis of the PMVE chain at the tetrad level using the signal of the backbone CH_2-group seem to be impossible due to its overlapping with the signal of the backbone quaternary carbon (at 48.0 ppm).

CONCLUSIONS

The stereochemical structure of PMVE was studied by one-dimensional ^{13}C n.m.r. spectroscopy. It was assumed that the chemical shift dispersion among the various sequences observed for the aromatic carbon signal and for signals of methyl carbons attached to the phenyl ring arises mainly from the influence of the neighbouring conjugated blocks, formed by the aromatic ring and part of the pyran cycle. On the contrary, stereosequence-dependent chemical shifts of the ester carbonyl signal result from the γ-gauche effect. The sensitivity of the aromatic and the methyl carbon signals to the stereosequences was found to depend upon the steric constraint (due to the vicinity of the CH_3-group and/or the chiral centre of the cycle bearing bulky substituents). This steric factor was assumed to be prevalent hindering the extension of the carbons of the central unit to the maximum shielding zone of the neighbouring conjugated groups and/or 'blocking' their influence. The microstructure analysis of PMVE chain carried out at the triad and pentad level showed that the chain propagation of PMVE prepared by radical polymerization could be described by Bernoullian statistics, with a clear tendency towards the syndiotactic structure containing isolated meso placements. Number-average sequence lengths for meso and racemic additions are 1.4 and 3.4, respectively.

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