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Microstructural analysis of poly(glycidyl methacrylate) by ^{1}H and ^{13}C NMR spectroscopy

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Abstract

The stereochemical configuration of poly(glycidyl methacrylate) has been analyzed by ^{1}H and ^{13}C NMR spectroscopy. Homopolymers prepared by free radical polymerization in solution and in bulk at 80°C are predominantly syndiotactic and follow the Bernoullian distribution of tactic sequences with isotactic parameters, $\sigma(s) = 0.24$ and $\sigma(b) = 0.27$, very close to that of the free radical polymerization in solution of methyl methacrylate, $\sigma(s) = 0.23$. This information is of primary importance for polymer characterization, but it also provides knowledge about the reaction mechanism. © 2001 Published by Elsevier Science Ltd.

Keywords: ^{13}C NMR spectroscopy; Microstructural analysis; Acrylic homopolymers

1. Introduction

The design and preparation of polymeric drugs for pharmacological applications are among the most interesting fields of research of new polymeric systems as biomaterials, mainly since Ringsdorf suggested a practical model of active polymeric systems in 1975 [1–4].

One of the most promising approaches is the synthesis of new polymeric drugs based on well-known pharmacons or drugs bound covalently to a macromolecular support [5]. These systems may display pharmacological activity by themselves or, alternatively, may be used as carriers for the pharmaceutical agent [2,5]. The main goals are to improve the duration of activity through the controlled release of the drug residue, to obtain a more cell-specific uptake (targeting effect) or to reduce the toxicity of the parent drug [6–8].

On the other hand, the biodegradative or hydrolytic behavior of the polymeric systems in physiological conditions depends predominantly on the chemical structure [9] but it has been widely recognized that the microstructure of polymeric chains, i.e. the distribution of monomeric sequences along copolymeric chains and the stereochemical configuration of the pseudoasymmetric carbons present in the repeat units along the macromolecular chains, drastically affects the kinetics and mechanism of the biodegradation process, which in addition can be controlled enzymatically [9,10].

Of all the available spectroscopic techniques for microstructural studies, high-resolution nuclear magnetic resonance (NMR) spectroscopy has proved to be one of the most versatile, informative and generally applicable in this field [11,12]. Its limitations are mainly dictated by the solubility of the polymer in an adequate solvent, by the correlation times that determine the lifetime of the nuclear spin states, and by the inhomogeneous broadening of peaks.

Glycidyl methacrylate (GM) has been homopolymerized in solution and the nature of poly(glycidyl methacrylate) is markedly affected by the mode of polymerization [13]. The microstructural study of poly(glycidyl methacrylate) prepared at 80°C in bulk and in solution of ethyl acetate using benzoyl peroxide as free radical initiator is detailed.

2. Experimental

2.1. Monomer and purification of materials

GM was distilled under reduced pressure from ionone; b.p. = 83°C. Methanol (Fluka AG) was distilled at normal pressure; b.p. = 65°C. Ethyl acetate (Fluka AG) was distilled at normal pressure; b.p. = 77°C. Benzoyl peroxide was purified by fractional crystallization from methanol; m.p. = 104°C.

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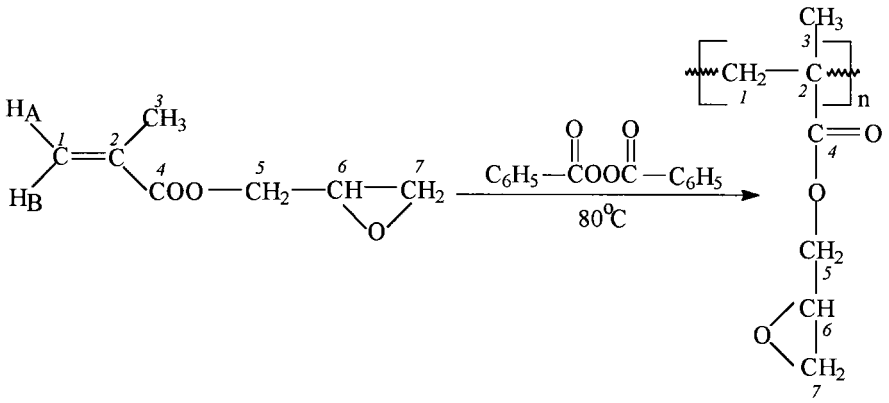


Fig. 1. Scheme of polymerization.

2.2. Polymerization

The monomer GM was polymerized at 80°C in bulk and in solution of ethyl acetate, [GM] = 1 mol/l, using benzoyl peroxide as free radical initiator. The reactions were carried out in Pyrex glass ampoules sealed at high vacuum. After polymerization for 8 h, the reaction mixture was poured into a large excess of methanol and the precipitated polymer was filtered off, washed with methanol and dried at reduced pressure at room temperature until constant weight.

2.3. Spectroscopic experiments

The monomer GM and homopolymers prepared were characterized by infrared (IR) and $^{1}H/^{13}C$ NMR spectroscopies. IR spectra of the monomer were recorded for a neat liquid between NaCl windows and in KBr pellets for homopolymers on an ATI MATTSON Genesis spectrometer. NMR spectra were recorded with a Bruker AC-250F spectrometer equipped with an ASPECT 3000 computer, at the frequencies of 250 MHz (^{1}H) and 62.89 MHz (^{13}C) at 70°C. The homopolymers were dissolved in deuterodimethylsulphoxide-d_6 (DMSO-d_6), in concentrations ranging from 12 to 15% (w/v). Tetramethylsilane (TMS) was used as internal reference and chemical shifts were reported in ppm. The nature of each carbon atom was determined using the DEPT spectral editing technique, with proton pulses at $\theta = 135°$ and $\theta = 90°$, respectively. In the case of homopolymer samples, ^{13}C NMR spectra were obtained with suppression of NOE using an inverse gated-decoupling scheme with relaxation delay of 5 s, a condition which ensures the complete relaxation of all the ^{13}C nuclei studied. The relative signal intensities were measured from the integrated signal areas, calculated by means of an electronic integrator and by triangulation and planimetry.

3. Results and discussion

The homopolymers were characterized by IR, ^{1}H and ^{13}C NMR spectroscopies. Both samples were investigated under similar conditions, and hydrogen and carbon atom numbers cited in all tables correspond to the structure in Fig. 1.

Table 1 summarizes the fundamental IR frequencies and band assignments of the monomer GM and the homopolymers. In the homopolymers IR spectra the band at 1729 cm^{-1} together with the strong broad absorption centered at 1147 cm^{-1} suggest an ester group. The C=O vibration shows a relatively large shift with respect to the vibration in the monomer. The olefinic band indicated by the sharp absorption at 3062 and 1637 cm^{-1} in the IR spectrum of the monomer is absent in the spectra of the homopolymers. The band in 909 cm^{-1} corresponds to the epoxy group in agreement with the literature reports [14].

The chemical shifts and signal assignments of the ^{1}H and

Table 1
IR frequencies (cm^{-1}) and band assignments of monomer (GM) and homopolymers (b: bulk polymerization; s: solution polymerization)

GM		PGM (b)		PGM (s)	
ν (cm^{-1})	Assignments	ν (cm^{-1})	Assignments	ν (cm^{-1})	Assignments
3062	ν_{Csp^2-H}	–	–	–	–
2994	ν_{C-H}	2997	ν_{C-H}	2998	ν_{C-H}
1720	$\nu_{C=O}$	1729	$\nu_{C=O}$	1730	$\nu_{C=O}$
1637	$\nu_{C=C}$	–	–	–	–
1379	δ_{C-H}	1390	δ_{C-H}	1389	δ_{C-H}
1170	ν_{C-O-C}	1147	ν_{C-O-C}	1149	ν_{C-O-C}
909	ν_{epoxi}	905	ν_{epoxi}	907	ν_{epoxi}

Table 2
^{1}H and ^{13}C NMR chemical shifts, δ (ppm), and signal assignments of PGM(b) and PGM(s) in DMSO-d_6 at 70°C (b): bulk polymerization (s): solution polymerization

^{13}C NMR	PGM(s) δ (ppm)	PGM(b) δ (ppm)	^{1}H NMR δ (ppm)	PGM(s) δ (ppm)	PGM(b) δ (ppm)
C_4	175.9	176.3	–	–	–
	175.6	176.0			
	175.2	175.3			
	175.0	174.9			
C_5	64.7	64.7	H_5	3.78	3.81
			H_5'	4.25	4.24
C_1	52.4	52.7	H_1	1.80–2.00	1.80–2.00
C_6	47.8	47.7	H_6	3.20	3.19
C_2	44.7	44.6	–	–	–
	44.2	44.2			
	43.9	43.9			
C_7	43.1	43.1	H_7	2.60	2.61
			H_7'	2.80	2.80
C_3	20.3	20.5	CH_3	0.93	0.95
	18.0	18.0		1.07	1.08
	16.4	16.4		1.29	1.29

^{13}C NMR spectra are summarized in Table 2. All the resonance signals have been assigned to the corresponding atoms according to the chemical structure drawn in Fig. 1.

The assignments have been made by comparison with spectra of analogous chemical groups taken from the literature [12,15–17] and of the basis of DEPT spectra for the carbon atoms and are in agreement with a prior report of Hunter and Price [13]. The α-CH_3 groups in both ^{1}H and ^{13}C NMR spectra, quaternary and carbonyl carbons of methacrylic ester groups in ^{13}C NMR present complex patterns which have been analyzed in terms of the content of different stereochemical sequences. The ^{1}H and ^{13}C NMR spectra are practically identical and have broad signals as correspond to high molecular weight compounds. The spectral signals of the PGM(b) are broader than the PGM(s) signals due to the bulk reaction producing higher molecular weight polymers.

The stereochemical configuration of monomeric units along the macromolecular chains has been analyzed by ^{1}H and ^{13}C NMR spectroscopy. Fig. 2 shows the expanded ^{1}H NMR spectrum of the α-methyl groups. The resonance signal of the α-CH_3 splits into three well resolved peaks at 0.93, 1.07, and 1.29 ppm, respectively, which have been assigned to isotactic (*mm*), heterotactic (*mr* + *rm*) and syndiotactic (*rr*) triads in order of increasing field, in a similar way to the assignment of the α-CH_3 resonance signals for poly(methyl methacrylate) (PMMA) by Bovey [18]. It is observed that the differences in chemical shifts between the two signals, ($\delta mm - \delta mr$) = 0.14 ppm and ($\delta rm - \delta rr$) = 0.18 ppm, are very close to that of the PMMA (= 0.15 ppm).

Fig. 3 shows the α-CH_3 resonance pattern of ^{13}C NMR spectrum of PMG(s) as example. The α-CH_3 groups are also sensitive to the stereochemical configuration in sequences of triads, giving three well-resolved peaks assigned, the same as the ^{1}H NMR spectra, to *mm*, *rm* + *mr* and *rr* tactic

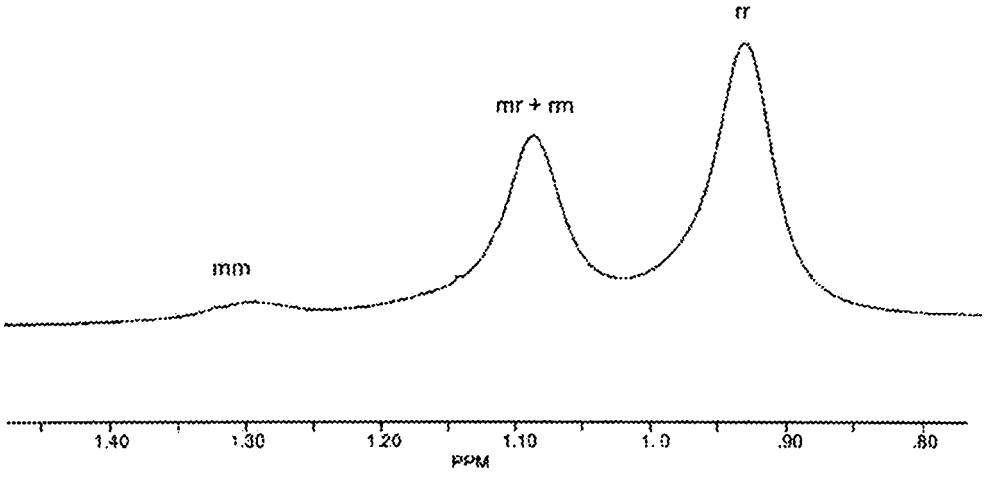


Fig. 2. Expanded ^{1}H NMR spectrum of the α-methyl groups of PGM in DMSO-d_6.

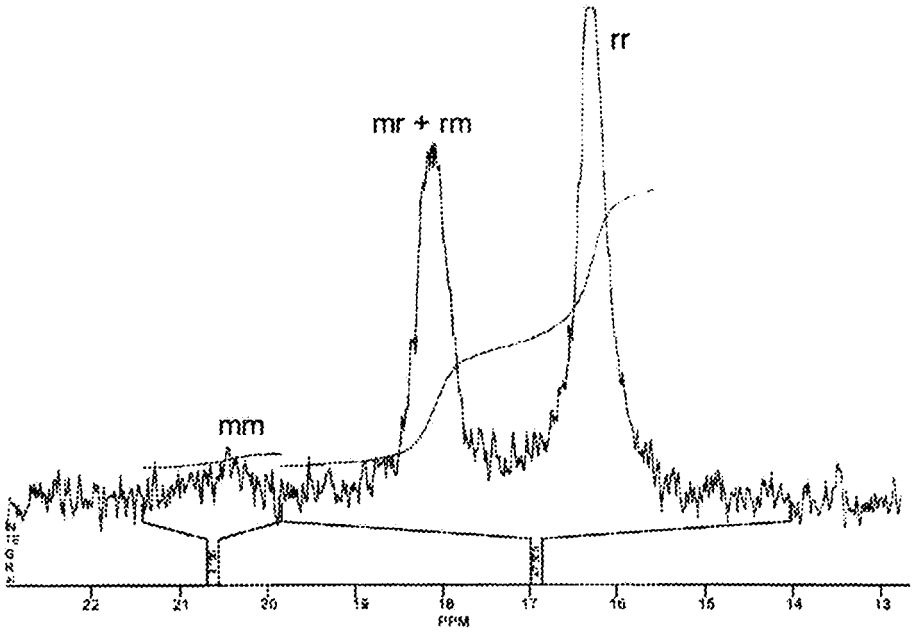


Fig. 3. Expanded ^{13}C NMR spectrum of the α-methyl groups of PGM in DMSO-d_6.

sequences in order of increasing field. As in the ^{1}H NMR spectra, there are several interesting differences between the corresponding resonance signals. In this way, we can see that $(\delta mm - \delta mr) = 2.5$ ppm and $(\delta rm - \delta rr) = 1.8$ ppm, very close to that of PMMA (2.0 ppm). However, the resonance signal assigned to isotactic mm sequences has practically the same chemical shifts for both homopolymers, 20.5 ppm. This means that the α-CH_3 side group in isotactic sequences shows very little sensitivity to the ester group, which is reasonable since the diamagnetic carbonyl centers are as far as possible from the α-CH_3 group of the central unit in the triad.

Tacticity is one of the most valuable parameters obtained from NMR spectra and the stereochemical assignments of ^{1}H and ^{13}C NMR spectra of various vinyl polymers has been established [12]. Reliability of signal intensity is of prime importance in the determination of tacticity by NMR spectroscopy. In the case of ^{13}C NMR spectra, they were

Table 3
Molar fraction of isotactic (*mm*), heterotactic (*mr* + *rm*) and syndiotactic (*rr*) triads determined from various resonance signals. Molar fraction of meso (*m*) and racemic (*r*) dyads calculated from triads

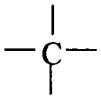
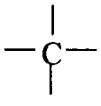
Triads	*mm*		*rm* + *mr*		*rr*	
	PGM(s)	PGM(b)	PGM(s)	PGM(b)	PGM(s)	PGM(b)
α-CH_3 (^{1}H NMR)	0.07	0.08	0.40	0.40	0.56	0.52
α-CH_3 (^{13}C NMR)	0.06	0.07	0.36	0.43	0.60	0.50
	0.06	0.08	0.37	0.40	0.59	0.52
Average	0.06	0.08	0.38	0.41	0.58	0.51
Dyads (calculated from triads)	*m*		*r*			
	PGM(s)	PGM(b)	PGM(s)	PGM(b)		
α-CH_3 (^{1}H NMR)	0.26	0.28	0.75	0.72		
α-CH_3 (^{13}C NMR)	0.24	0.26	0.77	0.71		
	0.24	0.28	0.77	0.72		
Average	0.24	0.27	0.76	0.72		

Table 4
Comparative stereochemical parameters of the free radical polymerization of GM(b), GM(s) and MMA

Parameter	GM(s)	GM(b)	MMA
Addition probabilities			
p_m	0.24	0.27	0.23
p_r	0.76	0.72	0.77
p_{mm}	0.06	0.08	0.05
$p_{r/m} + p_{m/r}$	0.38	0.41	0.35
p_{rr}	0.58	0.51	0.59
Conditional probabilities			
$p(m/m)$	0.25	0.29	0.22
$p(r/r)$	0.76	0.71	0.77
$p(m/r)$	0.25	0.29	0.23
$p(r/m)$	0.76	0.72	0.78
$p(m/r) + p(r/m)$	1.01	1.01	1.01

obtained using a gated-decoupling scheme with suppression of NOE.

The values of molar fractions of tactic sequences have been determined in three independent ways from the relative intensities of the α-CH_3 signals in both ^1H and ^{13}C NMR spectra and quaternary carbon atoms and collected in Table 3 and, as shown, they are very similar, illustrating the consistency of the procedure.

All data collected in Table 3 have been used to calculate the average value of molar fractions of *mm*, *mr* + *rm* and *rr* tactic triads, with the homopolymers being predominantly syndiotactic, independent of the polymerization medium (bulk or solution). From the average values of the molar fractions of tactic triads, the statistical parameters were determined. These are collected in Table 4 together with methyl methacrylate data for comparative purposes.

The conditional probabilities for isotactic and syndiotactic additions to meso or racemic growing chain ends, $p(i/j)$, $i, j = m, r$ (i refers to the relative stereochemical configuration of the chains and j to the adding monomer), indicate a random distribution of the meso and racemic dyads along the polymer chains, since the sum $p(m/r) + p(r/m)$ is very close to unity [18]. Therefore, the stereochemical distribution of monomeric units along the macromolecular chains is consistent with Bernoullian statistics, with a single parameter describing the probability for isotactic placement, defined by Bovey and Tiers [19] as the isotacticity parameter, $\sigma = p_m(\mathrm{s}) = 0.24$ and $\sigma = p_m(\mathrm{b}) = 0.27$, very close to that calculated for methyl methacrylate, $\sigma = 0.23$.

Also interesting is the analysis of the so-called *Z*-parameter [20], which is very sensitive to variation of the propagation mechanism from Bernoullian statistic, principally when the polymers obtained are predominantly, in this case, syndiotactic or isotactic [21]. The fact that this parameter has a value very close to unity makes it clear that the propagation mechanism of the stereocontrol of the polymerization process is Bernoullian.

The molar fractions of (*m*) and (*r*) dyads calculated considering the Bernoullian characters of the propagation step are collected in Table 3.

4. Conclusions

The free radical polymerization of GM in bulk and in solution at 80°C gives predominantly syndiotactic homopolymers and the radical propagation leads to the formation of macromolecular chains with a stereochemical distribution of tactic sequences according to Bernoullian statistics. The stereochemical parameters of the free radical polymerization of GM in bulk and in solution calculated from molar tactic triads are very close to that of the free radical polymerization of methyl methacrylate in solution.

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