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Stereochemical Configuration of Poly(methyl α-(*p*-chlorobenzyl)acrylate) and Poly(methyl α-(*p*-methoxybenzyl)acrylate) Synthesized by Radical Polymerization

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ABSTRACT: Methyl α-(*p*-chlorobenzyl)acrylate and methyl α-(*p*-methoxybenzyl)acrylate have been synthesized and polymerized at temperatures between 40 and 90 °C in benzene solutions with AIBN as the initiator. The stereochemical parameters of both polymers have been determined from the analysis of the ^{1}H NMR OCH_3 and ^{13}C NMR C=O and aromatic C* resonance signals. The results obtained indicate that the mechanism of the stereochemical additions of monomers to polymeric chain ends deviates from classical Bernoullian statistics.

Introduction

It has been widely demonstrated that the syndiotactic and isotactic additions in the propagation step of free radical polymerization are markedly influenced by the chemical structure of substituents on the olefinic carbons.[1-3] In this sense, several authors[4-7] have stated that the presence of an α-CH_3 group in vinyl and acrylic monomers gives rise to polymers with atactic or syndiotactic stereochemical configurations. Other organic groups such as α-chloro or α-cyano[1] give rise to the formation of polymers with a predominant syndiotactic stereostructure. However, larger substituents in the α-position such as α-ethyl, α-*n*-propyl, α-phenyl, etc.[8] seem to favor the formation of atactic polymers.

In an earlier report[9] we analyzed the stereochemical configuration of poly(methyl α-benzylacrylates) prepared be free radical polymerization at several temperatures, being predominantly syndiotactic. However, the formation of isotactic sequences was favored in comparison with poly(methyl methacrylate) prepared under the same experimental conditions in such a way that the mechanism for the propagation step of the free radical polymerization of methyl α-benzylacrylate initiated by AIBN could be fitted to the first-order Markov model.

To obtain more information about the influence of the chemical structure of this kind of monomer on stereoregulation in the propagation step of the free radical polymerization, this article deals with the determination of the stereochemical configuration of polymers derived from methyl α-(*p*-chlorobenzyl)acrylate (CLBAM) and methyl α-(*p*-methoxybenzyl)acrylate (MBAM). The results obtained are compared with those of poly(methyl α-benzylacrylate) (BAM) and poly(methyl methacrylate).

Experimental Section

Methyl α-(*p*-chlorobenzyl)acrylate and methyl α-(*p*-methoxybenzyl)acrylate were prepared from the condensation of dimethyl malonate with the corresponding para-substituted benzyl chloride as described elsewhere.[10]

Polymerizations were carried out in sealed glass ampules under high vacuum with benzene as the solvent and 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator. The reaction temperature was regulated between 40 and 90 ± 0.05 °C in a thermostatic bath. The polymers were isolated by pouring the solution into excess methanol (CLBAM) or heptane (MBAM) and washing and drying the samples to constant weight. The polymers were analyzed by ^{1}H NMR (Varian EM-390, 90 MHz) and ^{13}C NMR (Bruker WP 80 SY, 20.15 MHz) spectroscopies using nitrobenzene, deuterated chloroform, and deuterated acetone as the solvents. The spectra in acetone or chloroform solutions were recorded at 60 °C and those in nitrobenzene at 120 °C. The stereochemical parameters were calculated from the areas of appropriate signals measured by triangulation and planimetry.

Results and Discussion

As we have stated previously,[9] the ^{1}H NMR spectrum of poly(BAM) recorded in deuterated chloroform does not give useful tacticity information because of the poorly resolved methoxy proton signals. However, the resonance pattern of methoxy protons splits into three rather well-resolved peaks at 3.47, 3.60, and 3.70 ppm from HMDS when nitrobenzene is used as the solvent. The splitting of the methoxy proton resonances in the presence of aromatic solvents has been explained by several authors[11,12] by taking into account the possible differences in the orientation of the methoxy groups with respect to the π-electron system of the aromatic ring of the solvent molecules for each of the three kinds of tactic triad stereosequences.

In a similar way, Figure 1 shows that the methoxy proton resonance pattern of poly(CLBAM) in chloroform solution is not adequately resolved to evaluate the relative concentration of tactic triads, but the spectra recorded in deuterated acetone or nitrobenzene contain well-resolved peaks at 3.54, 3.66, and 3.77 ppm from HMDS. These resonances have been assigned by comparison with the spectra of poly(BAM)[9] and poly(methyl methacrylate) recorded in aromatic solvents[13] to rr, (rm + mr), and mm triads, respectively. This assignment has been verified by the analysis of the decoupled ^{13}C NMR spectrum recorded

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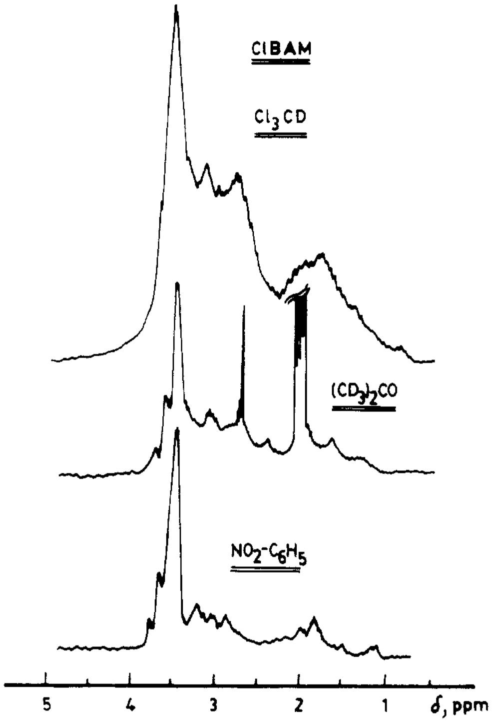

Figure 1. Expanded ^1H NMR spectra of poly(methyl α-(*p*-chlorobenzyl)acrylate) in different solvents.

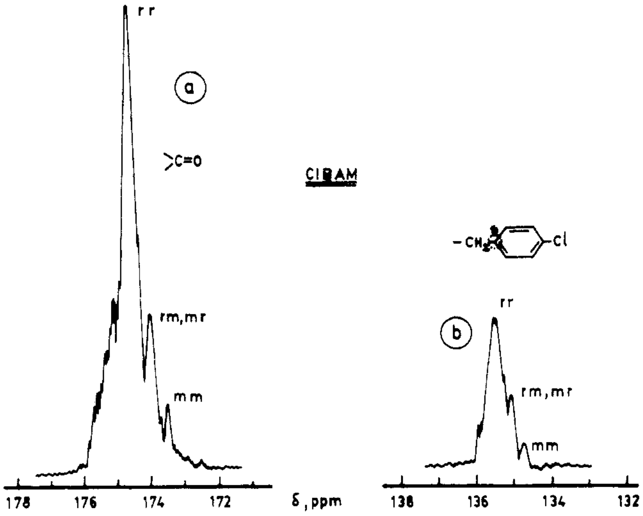

Figure 2. ^{13}C NMR decoupled spectrum of poly(methyl α-(*p*-chlorobenzyl)acrylate) synthesized by radical polymerization at 40 °C: (a) carbonyl signals; (b) aromatic carbon C* signals.

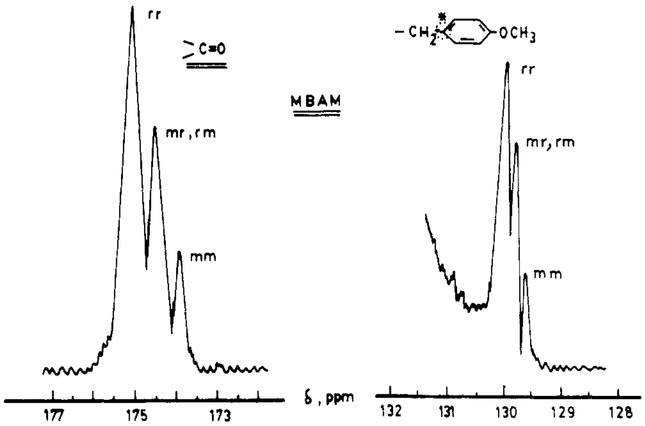

Figure 3. ^{13}C NMR decoupled spectrum of poly(methyl α-(*p*-methoxybenzyl)acrylate) synthesized by radical polymerization at 40 °C.

Table I
Tactic Triad Fractions of Poly(methyl α-(*p*-chlorobenzyl)acrylate) Synthesized by Radical Polymerization at 40 °C

	fraction		
signal	mm	(mr + rm)	rr
(^1H) OCH_3	0.08_9	0.24_5	0.66_5
(^{13}C) C═O	0.08_5	0.23_0	0.68_5
(^{13}C) C*	0.09_2	0.25_7	0.65_1

in deuterated chloroform, which contains resonance signals for the carbonyl carbon that are split into three peaks at 174.9, 174.2, and 173.5 ppm from Me_4Si, as shown in Figure 2a. On the basis of similar results for poly(BAM),[9] those reported by Lenz et al.[14] for poly(alkyl α-(phenoxymethyl)acrylates) and those reported by Inoue et al.[15] for poly(methylmethacrylate), these peaks have been assigned to syndiotactic, heterotactic, and isotactic triads in order of increasing field.

The resonance of the C* carbon in the phenyl ring (Figure 2b) is also split into three peaks at 135.6, 135.2, and 134.8 ppm from Me_4Si, which have been assigned to rr, (mr + rm), and mm triads in order of increasing field, according to similar assignments for poly(BAM)[9] and for several poly(alkyl α-(phenoxymethyl)acrylates).[14] Isotactic, heterotactic, and syndiotactic triad fractions of poly(CLBAM) synthesized at 40 °C are quoted in Table I. The values calculated from the OCH_3 resonances have been averaged from the spectra recorded in acetone-d_6 and nitrobenzene. Very similar results have been obtained from the analysis of polymers prepared at higher temperatures (60 and 80 °C), so that there is no variation of tacticity in this temperature interval.

The tacticity of poly(MBAM) cannot be evaluated from ^1H NMR spectra because of the overlapping of the *p*-methoxy and the methoxy ester resonance signals. However, it is noteworthy that the *p*-methoxy group gives a sharp singlet centered at 3.73 ppm from HMDS independently of the solvent used, whereas the methoxy ester group gives a broader signal centered at 3.42 ppm when chloroform or acetone are used as solvents but is shifted downfield (3.55 ppm) in nitrobenzene. This fact seems to indicate that the nitrobenzene molecules interact selectively with the methoxy ester group, which supports the earlier suggested idea that nitrobenzene molecules in the vicinity of methoxy ester groups are oriented in such way that the aromatic ring of the solvent lies as far as possible from the phenyl rings and the carbonyl groups in the polymer. In this sense, several authors[16] have indicated that for polymers prepared from methyl α-phenoxymethacrylate, methyl α-cresoxymethacrylate and methyl α-(*p*-nitrophenoxy)methacrylate the NMR resonance signals of the methoxy protons are shifted toward lower magnetic field in the order of phenoxy-, *p*-cresoxy-, and *p*-(nitrophenoxy)methacrylates.

The molar fraction of isotactic, heterotactic, and syndiotactic triads for poly(MBAM) have been determined from its decoupled ^{13}C NMR spectrum recorded in deuterated chloroform, since the carbonyl carbon and the *C aromatic carbon are sensitive to configurational differences in the polymer backbone in terms of triads. The expanded spectra of these carbon resonances are shown in Figure 3. As in the case of poly(BAM) and poly(ClBAM), the three carbonyl carbon resonances that appear at 175.2, 174.5, and 173.8 ppm from Me_4Si have been assigned to rr, (rm + mr), and mm triads, respectively. In a similar way, the resonance signals at 130.0, 129.8, and 129.6 ppm have been assigned to the aromatic ring carbon *C in rr, (mr + rm),

Table II
Tactic Triad Fractions of Poly(methyl α-(*p*-methoxybenzyl)acrylate) Synthesized by Radical Polymerization at 40 °C

signal	fraction		
	mm	(mr + rm)	rr
(^{13}C) C=O	0.09_1	0.32_8	0.58_1
(^{13}C) C*	0.09_8	0.32_6	0.57_5

Table III
Stereochemical Parameters of Methyl α-(*p*-Substituted-benzyl)acrylate Polymers Prepared by Radical Polymerization at 40 °C[a]

monomer	CLBAM	MBAM	BAM
rr	0.66_7	0.57_8	0.54_8
(rm + mr)	0.24_4	0.32_7	0.31_8
mm	0.08_9	0.09_5	0.13_4
m	0.21_1	0.25_9	0.29_3
r	0.78_9	0.74_1	0.70_7
$p(\mathrm{m/m})$	0.42_2	0.36_7	0.45_7
$p(\mathrm{r/r})$	0.84_5	0.78_0	0.77_5
$p(\mathrm{r/m})$	0.57_8	0.63_2	0.54_3
$p(\mathrm{m/r})$	0.15_5	0.22_0	0.22_5
$p(\mathrm{m/r}) + p(\mathrm{r/m})$	0.73_3	0.85_2	0.76_8
ρ_i	1.36	1.17	1.30
η_s	1.07	1.05	1.10

[a] Polymerization temperature was 40 °C.

and mm triads, respectively.

Isotactic, heterotactic, and syndiotactic triad fractions of poly(MBAM) synthesized at 40 °C are listed in Table II. Similar results have been obtained from the analysis of spectra of polymers prepared at 60, 80, and 90 °C, so that as in the case of poly(BAM)[9] and poly(CLBAM) there are not any appreciable tacticity differences in a temperature interval from 40 °C to the ceiling temperature for each one of these monomers.

Table III shows the average values of rr, (mr + rm), and mm triad fractions for poly(CLBAM) and poly(MBAM) together with those of poly(BAM). From these values have been calculated the molar fractions of racemic and meso diads as well as the statistical parameters expressed as conditional probabilities for meso and racemic additions of monomers to meso or racemic growing chain ends, p(.../...). The values obtained indicate that all three polymers are predominantly syndiotactic, the syndiotacticity increasing in the order CLBAM > MBAM > BAM. However, the molar fraction of heterotactic triads (mr + rm) of poly(CLBAM) is quite different from those of poly(MBAM) and poly(BAM).

In order to test the polymerization mechanism it is useful to analyze the statistical parameters in terms of conditional probabilities for meso and racemic additions of monomer molecules to polymeric chain ends. In this sense, it has been widely recognized[17] that racemic diads are thermodynamically slightly favored over meso diads and the free energy differences between meso and racemic additions in the propagation step of the radical process are so small that the formation of stereosequences must be kinetically controlled. Thus, the stereoregularity in radical polymerization is controlled by the differences in the activation energy for the insertion of a monomeric unit in the growing chain. The results quoted in Table III show that the racemic additions $p(\mathrm{r/r})$ and $p(\mathrm{r/m})$ are favored against meso additions, independently of the stereochemical configuration of the polymer chain end. However, the meso addition to isotactic growing ends as expressed by the conditional probability $p(\mathrm{m/m})$, seems to be slightly lower for CLBAM than BAM but higher than MBAM, and in all cases this parameter is sensibly higher than that of methyl methacrylate, $p(\mathrm{m/m}) = 0.232$.[18]

These results seem to indicate some specific interactions between the aromatic ring, the carbomethoxy groups of the active growing end, and the reactant, which could have polar as well as steric origin, since the phenyl aromatic rings of BAM molecules adding to the growing radicals might be relatively oriented to give the lowest electrostatic interactions with the carbomethoxy groups. In the case of the *p*-chloro derivative, an additional polar contribution can be expected because of the dipolar character of the Cl–C bond. Also the steric hindrance will be higher than for BAM since the chlorine atom has a van der Waals radius of 1.8 Å, slightly lower than that for a methyl group, with a radius of 2.0 Å.[22] The lowest value of $p(\mathrm{m/m})$ for the *p*-methoxy derivative could be related with the additional steric hindrance as compared with BAM.

On the other hand, the kinetic study of the free radical polymerization of BAM, CLBAM, and MBAM in 5 mol/L benzene solution at several temperatures has indicated that the ceiling temperatures of these monomers under the experimental conditions mentioned above are approximately 67 °C for BAM[10] 84 °C for ClBAM, and 95 °C for MBAM,[21] and the number-average molecular weights of the polymers prepared at 40 °C are close to 5000 in all three cases. The differences in ceiling temperatures of these monomers have been attributed to differences in entropic factors rather than to differences in enthalpic ones.[21] A temperature of 40 °C is rather close to the corresponding ceiling temperature of the monomers, and a possible effect of the propagation–depropagation equilibrium on the stereochemistry of the addition reactions cannot be rejected.

As we have reported previously,[9] from a mechanistic point of view, the isotactic and syndiotactic additions of methyl α-benzylacrylate to growing chain ends seemed to deviate from Bernoullian statistics and could be fitted to the first-order Markov model. In light of the results quoted in Table III, similar behavior can be expected for the polymerization of CLBAM and MBAM, since the $p(\mathrm{m/r}) + p(\mathrm{r/m})$ values for the three monomers are different from unity and the persistance ratios for isotactic sequences as defined by Reinmöller and Fox[19] are greater than unity. In this sense, Ito et al.[20] have reported an interesting study by NMR analysis of the tacticity of several poly(alkyl α-chloroacrylates), concluding that the stereochemical structures of isotactic poly(methyl α-chloroacrylates) were found to be described by first-order Markovian statistics, while those of the syndiotactic polymers followed Bernoullian statistics. Similar results have been reported by Lenz et al.[12] for polymers derived from methyl, ethyl, and isopropyl chloroacrylates. Moreover, Lenz et al.[12] in the study of predominantly syndiotactic poly(alkyl α-chloroacrylates) prepared by free radical polymerization have found values of $\rho_i = 1.10$ for ethyl and $\rho_i = 1.43$ for isopropyl. They suggest that the great divergence from Bernoullian statistics of the isopropyl derivative could be related with the low molecular weight of the corresponding polymer and with the poor accuracy of data taken from poorly resolved NMR spectra. However, it is clear that also there is a little divergence from Bernoullian statistics for methyl and ethyl derivatives, as indicated by the persistence ratio values.

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Stereochemical Selectivity during the Formation of $CH_2RCH_2CHRCH_2$– Branches in the Free Radical Initiated Polymerization of Monosubstituted Vinyl Monomers

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ABSTRACT: Isolated butyl branches in low-density polyethylene are formed by an intrachain radical rearrangement that is followed by repeated addition of ethylene without further rearrangement. The analogous intramolecular radical rearrangement in a monosubstituted vinyl chain that is terminated by $-CHRCH_2CHRCH_2\dot{C}HR$, followed by the repeated addition of $CHR{=}CH_2$, produces an isolated $-CH_2CHRCH_2CH_2R$ branch. The probability of this rearrangement is strongly influenced by the stereochemistry of the diad denoted by asterisks in the fragment $-CHR^*CH_2CHR^*CH_2\dot{C}HR$. The rearrangement is more likely in chains that have a meso diad at this position. There is an increase in selectivity for meso diads as η increases. Here η is the first-order statistical weight for a trans placement at a bond in the main chain.

The free radical initiated polymerization of ethylene at high pressure produces a branched polymer. Intermolecular hydrogen atom abstraction is responsible for the formation of long branches, which can contain a number of bonds comparable with that found in the main chain.[1,2] Intramolecular hydrogen atom abstraction via a cyclic intermediate is the crucial step in the formation of short branches.[3] The intramolecular radical rearrangement can be written as

$$-(CH_2)_kCH_2(CH_2)_{j-1}\dot{C}H_2 \rightarrow -(CH_2)_k\dot{C}H(CH_2)_{j-1}CH_3 \tag{1}$$

The butyl branch is the most frequently reported short branch in low-density polyethylene,[4-14] but other short branches have also been identified.[4-15] An isolated butyl branch is formed if $j = 4$ and the intramolecular radical rearrangement in eq 1 is followed by addition of several molecules of ethylene without further rearrangement.[3,16] A complex branch can be formed if a second intramolecular radical rearrangement takes place after the addition of only one or two molecules of ethylene.[16-18]

An intramolecular radical rearrangement with $j = 4$ is depicted in a somewhat different manner in Figure 1. The hydrogen atom that will be abstracted is denoted by H*. Figure 1 and eq 1 describe the same intramolecular radical rearrangement if R = H and $j = 4$. However, if R ≠ H, Figure 1 depicts intramolecular radical rearrangements in monosubstituted vinyl polymers. For example, if R = Cl, Figure 1 describes the intramolecular radical rearrangement that leads to the formation of 2,4-dichloro-*n*-butyl branches, which are second in occurrence only to chloromethyl branches in poly(vinyl chloride).[19] The first defined diad at the growing chain end in Figure 1A is a meso diad, but it is replaced by a racemic diad in Figure 1B.

The R substituent affects the rates of the two intramolecular radical rearrangements because it alters the inherent reactivity of H* and also influences the probability that the chain end will adopt a conformation that brings the reactive chain end and H* into a suitable juxtaposition. Both factors need be considered in a comparison of two chains that have different R substituents. Conformational control is the only important factor if the interest is in the relative rates of the two intramolecular radical rearrangements under circumstances where both chains have the same R substituents. At issue is whether the stereochemical composition at the reactive chain end has an influence on the probability for the formation of an isolated $-CH_2CHRCH_2CH_2R$ branch. A rotational isomeric state analysis can easily demonstrate that the intramolecular radical rearrangement depicted in Figure 1A is generally favored over that in Figure 1B. The selectivity may be greater than a factor of 10.

Rotational Isomeric State Treatment

Configuration partition functions for the monosubstituted vinyl polymers are obtained with minor modification of the rotational isomeric state treatment developed by Flory et al.[20] The configuration partition functions are

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