Stereochemical Configuration of Poly(methyl α-benzylacrylate) Synthesized by Radical Polymerization

Julio San Román,* Enrique Lopez Madruga, and M. Angeles Lavia

Instituto de Plâsticos y Caucho (CSIC), Madrid-6, Spain. *Received May 23, 1983*

ABSTRACT: Methyl α-benzylacrylate has been polymerized at 40, 50, and 60 °C in benzene solutions with AIBN as initiator. From the analysis of OCH_3 resonance signals of ^1H NMR spectra recorded in nitrobenzene solutions and C=O and aromatic C* signals of ^{13}C NMR spectra recorded in deuterated chloroform, the isotactic, heterotactic, and syndiotactic triads have been calculated. The data obtained make it clear that the polymers obtained are predominantly syndiotactic and the tacticity observed is independent of the polymerization temperature in the experimental interval studied. However, the analysis of the conditional probabilities for isotactic and syndiotactic additions and the persistence ratios indicate that the propagation mechanism for the radical polymerization of methyl α-benzylacrylate is not Bernoullian. First-order Markov statistics have been fitted but not tested.

Introduction

In the free radical polymerization of vinyl monomers the syndiotactic and isotactic additions of monomers to polymeric radicals are influenced by the chemical structure of the substituents on the olefinic carbons.[1–3] In this sense, α,α-disubstituted olefinic monomers such as methyl methacrylate,[4] α-methylstyrene,[5] and phenyl methacrylate[6] usually give rise to syndiotactic polymers. The fraction of heterotactic triads in these products generally increases with increasing polymerization temperature.[6] Also the predominant syndiotactic structure of a great number of alkyl methacrylates[3] has been assumed to be due to syndiotactic propagation because of the repulsion between the α-CH_3 at the polymer end and that of the approaching monomer.[1] Alkyl acrylate[7] and acrylonitrile,[8] which have no α-CH_3 groups, do not give syndiotactic polymers by radical polymerization. However, Matsuzaki et al.[1] reported that the radical polymerization of methyl α-chloroacrylate yields polymers with a predominant syndiotactic stereostructure. The chlorine at the α-position controls stereoregularity similar to that of α-CH_3 in poly(methylmethacrylate). It has been reported[9] that large substituents at the α-position of acrylate monomers such as methyl α-phenyl acrylate favor the formation of atactic polymer.

Methyl α-benzylacrylate is a sterically hindered monomer that polymerizes by a free radical mechanism, giving rise to polymers of relatively low molecular weight.[10] The radical polymerization initiated by AIBN in benzene presents overall rates of 4.65×10^{-8} and 13.90×10^{-8} mol L^{-1} s^{-1} at 40 and 60 °C, respectively (sensibly lower than those of methyl methacrylate). The kinetic analysis of the polymerization of this monomer at several temperatures[10] shows that the ceiling temperature of polymerization is 67 ± 2 °C in a 5 mol L^{-1} benzene solution.

In order to study the effect of monomer structure on the stereoregularity of poly(methyl α-benzylacrylate) and the effect of temperature on the tacticity in a interval relatively close to the ceiling temperature, polymers prepared in the range 40–60 °C have been analyzed by ^1H and ^{13}C NMR spectroscopy.

Experimental Section

Methyl α-benzylacrylate (BMA) was prepared from the condensation of dimethyl malonate with benzyl chloride as described previously.[10]

Polymerizations were carried out in sealed glass ampules at high vacuum using benzene as solvent and 2,2′-azobis(isobutyronitrile) (AIBN) as initiator. The reaction temperature was regulated between 40 and 60 °C (±0.05 °C) in a thermostated bath. Polymers were isolated by pouring the solution into methanol and washing and drying the samples to constant weight.

Polymers were analyzed by ^1H NMR (Varian EM-390, 90 MHz) and ^{13}C NMR (Bruker WP80SY) spectroscopy with deuterated chloroform and nitrobenzene as solvents. The spectra obtained in chloroform solutions were recorded at 60 °C and those obtained in nitrobenzene at 120 °C. The molar fraction of tactic triads was calculated from the areas of the corresponding signals measured by triangulation and planimetry.

Results and Discussion

The ^1H NMR spectra of poly(methyl α-benzylacrylates) prepared by radical polymerization at 40, 50, and 60 °C recorded in deuterated chloroform solutions at 60 °C (Figure 1a) did not give useful tacticity information, since the methoxyl proton signals were too poorly resolved to interpret as isotactic, heterotactic, and syndiotactic triads. However, if nitrobenzene is used as solvent, the resonance of the methoxyl protons splits into three peaks at 3.47, 3.60, and 3.70 ppm from HMDS as shown in Figure 1b. Yuki et al.[9] have explained a similar behavior of polymers from methyl esters of α-phenyl-, α-ethyl-, and α-*n*-propylacrylates by considering that in nitrobenzene solutions the solvent molecules may orient in the vicinity of the methoxyl groups in such a way that the aromatic ring of the solvent lies as far as possible from the π-electron system of the phenyl ring and the carbonyl group in the polymer. This orientation is probably facilited by dipole–dipole interactions between the nitrobenzene molecule and the methoxyl group, which results in the clear separation of the three methoxyl signals.[9] The comparison of the relative chemical shifts with those of poly(methyl methacrylate) recorded in aromatic solvents[11] and poly(methyl α-phenylacrylate) recorded in nitrobenzene-d_5[9] permits us to assign these peaks to (mm), (mr + rm), and (rr) triads in order of increasing field. This assignment has been verified from the analysis of the ^{13}C NMR spectra and is consistent with that of the methoxyl signals of poly(methyl methacrylate) proton NMR spectra recorded in aromatic solvents.[11]

Effectively, the decoupled ^{13}C NMR spectra of poly(methyl α-benzylacrylate) recorded in deuterated chloroform present resonances for the carbonyl carbon that split into three peaks at 174.8, 174.4, and 174.0 ppm from Me_4Si as shown in Figure 2a. On the basis of similar results reported by Lenz et al.[12] for poly(alkyl α-(phenoxymethyl)acrylates) and those reported by Inoue et al.[13] for poly(methyl methacrylate), it is possible to assign the carbonyl carbon peaks to syndiotactic, heterotactic, and isotactic traids in order of increasing magnetic field. As shown in Table I, the relative intensities of carbonyl resonances from the ^{13}C NMR spectrum of polymer prepared at 50 °C are rather similar to those calculated from the

0024-9297/84/2217-1762$01.50/0

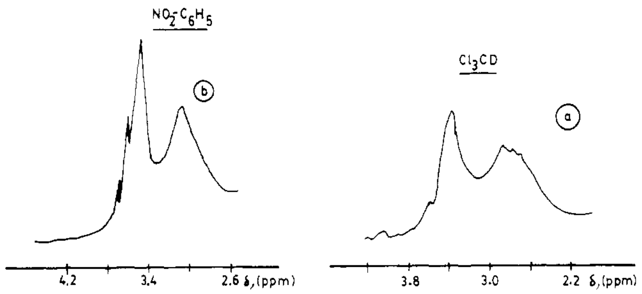

Figure 1. Expanded proton OCH_3 resonance signals of poly(methyl α-benzylacrylate) in (a) chloroform and (b) nitrobenzene solutions.

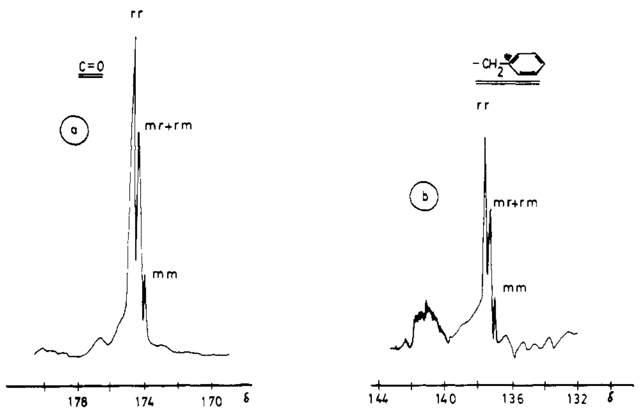

Figure 2. ^{13}C NMR decoupled spectrum of poly(methyl α-benzylacrylate) synthesized by free radical polymerization at 50 °C: (a) carbonyl signals; (b) aromatic carbon C* signals.

Table I
Iso-, Hetero-, and Syndiotactic Triad Fractions of Poly(methyl α-benzylacrylate) Synthesized by Free Radical Polymerization in Benzene at 50 °C

resonance signal	(mm)	(mr + rm)	(rr)
O-CH_3 (^1H)	0.12_1	0.32_7	0.55_2
C=O (^{13}C)	0.10_1	0.30_1	0.59_8
C* (^{13}C)	0.09_7	0.32_7	0.57_6

methoxyl resonances of the corresponding proton NMR spectrum. Moreover, the resonance of the C* carbon in the phenyl ring also splits into three peaks at 137.6, 137.2, and 136.8 ppm from Me_4Si, which have been assigned by comparison of the relative intensities of the peaks with those of the carbonyl peaks to the tactic triads in the order mentioned above with increasing magnetic field. Similar results have been reported by Lenz et al.[12] for poly(alkyl α-(phenoxymethyl)methacrylates). The results quoted in Table I show good agreement between values of the different tactic triads from the three resonance signals taken into consideration.

Polymers prepared at 40 and 60 °C also have been analyzed by ^1H and ^{13}C NMR spectroscopy and the averaged values calculated from the OCH_3, C=O, and C* signals for (rr), (mr + rm), and (mm) triad fractions for the three polymerization temperatures are quoted in Table II. The last column of this table shows the (rr), (mr + rm), and (mm) triad fractions of a poly(methyl methacrylate) prepared by free radical polymerization under similar experimental conditions and analyzed by ^1H NMR spectroscopy in benzene solution.[14] It is noteworthy, as shown by the data in this table, that the values obtained for each one of the triad fractions of polymers prepared at different temperatures are rather similar. Therefore no change in tacticity is observed for polymers prepared in the interval 40–60 °C, near the ceiling temperature. The insensitivity of stereosequences to polymerization temperature indicates that similar activation energies for syndiotactic and isotactic additions may be expected.

Table II
Stereochemical Parameters of Poly(methyl α-benzylacrylates) Prepared by Free Radical Polymerization at Several Temperatures

	temperature			
	40 °C	50 °C	60 °C	PMMA[a]
(rr)	0.54_8	0.57_5	0.57_1	0.58_4
(rm + mr)	0.31_8	0.31_8	0.31_8	0.37_0
(mm)	0.13_4	0.10_6	0.11_1	0.05_6
(m)	0.29_3	0.26_5	0.27_0	0.24_1
(r)	0.70_7	0.73_4	0.73_0	0.76_9
p(m/m)	0.45_7	0.40_0	0.41_1	0.23_2
p(r/r)	0.77_5	0.78_3	0.78_2	0.75_9
p(m/r)	0.54_3	0.60_0	0.58_9	0.76_8
p(r/m)	0.22_5	0.21_7	0.21_8	0.24_1
ρ_i	1.30	1.22	1.24	1.00
η_s	1.10	1.07	1.07	0.99

[a] Taken from ref 14.

The polymer chain stereoisomerism or stereochemical configuration is completely described by the stereosequence distribution, that is, by the specification of the probability of occurrence of every possible sequence of tactic placements formed by consecutive monomer units in the macromolecular chains. As has been widely reported,[3,15–20] in free radical polymerization the stereochemical configuration along the polymer chain is determined during the propagation step, which can be subdivided into two fundamental reactions (isotactic and syndiotactic propagations). To test particular polymerization statistics, it is convenient to express the polymer stereocomposition in terms of conditional probabilities. In this way, the isotactic or meso (m) and syndiotactic or racemic (r) dyads as well as the conditional probability of addition of monomers to propagating radicals, p(i/j) (i, j = m, r) are quoted in Table II. P(i/j) represents the probability that the monomer adds in j fashion to an i chain end. In light of results quoted in this table, the conditional probabilities of racemic and meso additions to racemic chain ends p(r/r) and p(r/m) seem to be rather similar for the poly(methyl α-benzylacrylate) prepared at 50 °C and poly(methyl methacrylate). However, the conditional probability of meso addition to an m chain end, p(m/m), is sensibly higher for α-benzyl-substituted than α-CH_3 monomers, whereas the conditional probability of racemic addition to meso chain ends seems to be lower for the α-benzyl-substituted monomer. These results indicate that in both cases, long syndiotactic sequences may be expected, but in the case of methyl α-benzylacrylate the formation of isotactic blocks seems to be favored as compared with poly(methyl methacrylate).

It is clear from these relations that there is an appreciable difference between the propagation mechanism of methyl α-benzylacrylate and methyl methacrylate, since the distribution of isotactic or syndiotactic placements is Bernoullian for poly(methyl methacrylate),[21,22] which means that

$$p(\mathrm{m}) = p(\mathrm{m/m}) = p(\mathrm{r/m})$$

$$p(\mathrm{r}) = p(\mathrm{r/r}) = p(\mathrm{m/r})$$

and so that

$$p(\mathrm{r/m}) + p(\mathrm{m/r}) = 1$$

whereas poly(methyl α-benzylacrylate) deviates, so that the stereosequence is not determined by a single parameter

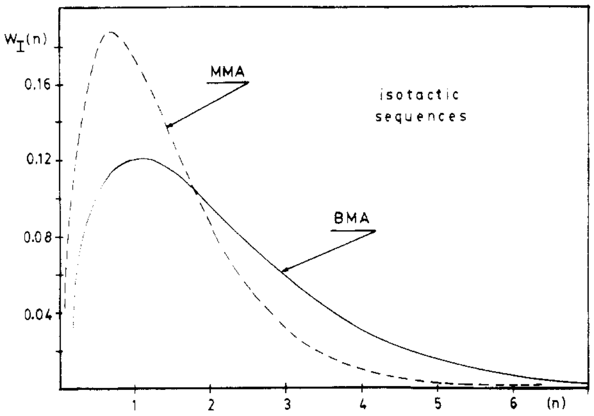

Figure 3. Distribution functions of isotactic sequences for poly(methyl methacrylate) (MMA) and poly(methyl α-benzylacrylate) (BMA) synthesized at 50 °C with AIBN as initiator.

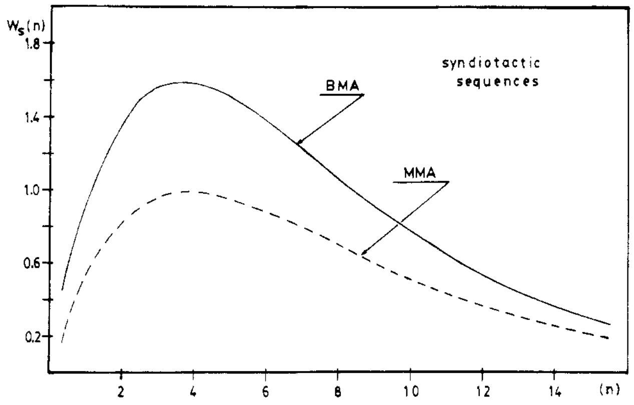

Figure 4. Distribution functions of syndiotactic sequences for poly(methyl methacrylate) (MMA) and poly(methyl α-benzylacrylate) (BMA) synthesized at 50 °C with AIBN as initiator.

for placement statistics. Moreover, the values of persistence ratios for isotactic (ρ_i) and syndiotactic (η_s) placements as defined by Coleman, Reinmöller, and Fox[23,24] indicate that poly(methyl α-benzylacrylate) does not follow simple Bernoullian statistics as manifested by the deviation from unity of ρ_i more than η_s.

The fact that the relation

$$\rho_i = [p(m/r) + p(r/m)]^{-1} \neq 1$$

indicates that from a stereochemical point of view, the propagation mechanism for the radical polymerization of methyl α-benzylacrylate may follow first-order Markov statistics,[21] although there is not experimental evidence since the NMR spectra do not present sufficient resolution to determine experimentaly the sequence distribution in terms of tetrads. Therefore the sequences are generated by propagation steps in which the adding monomer may be influenced by the stereochemistry of the growing chain end.

Figure 3 shows the weight fraction $W_i(n)$ of isotactic sequences of length n as a function of n for poly(methyl α-benzylacrylate) synthesized at 50 °C (similar results are obtained for the two other polymerization temperatures), together with that of poly(methyl methacrylate), taking into account the first-order Markov and Bernouillian statistical character of the corresponding propagation mechanism, respectively. It is clear that the distribution function for isotactic sequences is broader for poly(methyl α-benzylacrylate) than poly(methyl methacrylate). The probability of finding isotactic sequences of three or four units for α-benzyl-substituted acrylate is higher than for methyl methacrylate. However, the weight fraction of syndiotactic sequences of length n, $W_s(n)$, as a function of n represented in Figure 4, makes it clear that the distribution of syndiotactic sequences is rather similar for both polymers.

As concluding remarks we can state from the analysis of proton and carbon-13 NMR spectra of poly(methyl α-benzylacrylate) that the stereochemistry of the propagation step can be fitted to a first-order Markov model, with an effect more noticeable for polymer radicals ending in isotactic rather than syndiotactic dyads, and that the stereostructure of the polymer chain as manifested by the (mm), (mr + rm), and (rr) triad fractions is not temperature dependent in the interval of polymerization temperatures between 40 and 60 °C.

Acknowledgment. We thank the "Comision Asesora de Investigación Cientifica y Técnica" for support of this work.

Registry No. Poly(methyl α-benzylacrylate) (homopolymer), 91294-66-5.

References and Notes

(1) Matsuzaki, K.; Uryu, T.; Ito, K. *Makromol. Chem.* **1969**, *126*, 292.
(2) Odian, G. "Principles of Polymerization", 2nd ed.; Wiley-Interscience: New York, 1981.
(3) Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173.
(4) Ferguson, R. C. *Macromolecules* **1969**, *2*, 237.
(5) Brownstein, S.; Bywater, S.; Worsfold, D. S. *Makromol. Chem.* **1969**, *48*, 127.
(6) San Román, J.; Madruga, E. L. *Eur. Polym. J.* **1981**, *17*, 15.
(7) Matsuzaki, K.; Uryu, T.; Ishida, A.; Ohki, T.; Takeuchi, M. *J. Polym. Sci., Part A-1* **1967**, *5*, 2167.
(8) Matsuzaki, K. Uryu, T.; Okada, M.; Shiroki, H. *J. Polym. Sci. Part A-1* **1968**, *6*, 1475.
(9) Yuki, H.; Hatada, K.; Niinomi, T.; Hashimoto, M.; Oshima, J. *Polym. J.* **1971**, *2*, 629.
(10) Madruga, E. L.; San Román, J.; Lavia, M. A.; Fernandez-Monreal, M. C. *Macromolecules* **1984**, *17*, 989.
(11) Ramey, K. C.; Messick, J. *J. Polym. Sci., Part A-2* **1961**, *4*, 155.
(12) Lenz, R. W.; Saunders, K.; Balakrishnan, T.; Hatada, K. *Macromolecules* **1979**, *12*, 392.
(13) Inoue, Y.; Nishioka, A.; Cholo, R. *Polym. J.* **1971**, *2*, 535.
(14) San Román, J.; Madruga, E. L. *Eur. Polym. J.* **1982**, *18*, 481.
(15) Miller, R. L. *J. Polym. Sci.* **1962**, *56*, 375.
(16) Coleman, B. D.; Fox, T. G. *J. Polym. Sci. Part A* **1962**, *1*, 3183.
(17) Tsuruta, T.; Makimoto, T.; Kanai, H. *J. Macromol. Sci.* **1966**, *1*, 31.
(18) Miller, R. L.; Nielsen, L. *J. Polym. Sci.* **1960**, *46*, 303.
(19) Fordham, J. W. L. *J. Polym. Sci.* **1959**, *39*, 321.
(20) Pyun, C. W.; Fox, T. G. *J. Polym. Sci., Part A-2* **1971**, *9*, 615.
(21) Bovey, F. A. "High Resolution NMR of Macromolecules"; Academic Press: New York, 1972.
(22) Ramey, K. C.; Brey, W. S. *J. Macromol. Sci., Rev. Macromol. Chem.* **1967**, *C1*, 2, 263.
(23) Coleman, B. D.; Fox, T. G. *J. Chem. Phys.* **1963**, *38*, 1065.
(24) Reinmöller, M.; Fox, T. G. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1966**, *7*, 999.