Polymer Vol. 36 No. 18, pp. 3467–3472, 1995

0032-3861/95/$10.00+0.00

Study of the microstructures of phenyl and 4-fluorophenyl polyacrylates by ^{1}H and ^{13}C n.m.r. spectroscopy

B. Vázquez, M. Gurruchaga, I. Goñi and E. Narvarte
Departamento de Ciencia y Tecnología de Polímeros, Facultad de Química de San Sebastián, Apartado 1072, San Sebastián-20080, Spain

and J. San Román*
Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, 28006-Madrid, Spain
(Received 23 September 1994; revised 13 December 1994)

The microstructures of phenyl and 4-fluorophenyl polyacrylates were studied by 500 MHz ^{1}H and 125 MHz ^{13}C n.m.r. spectroscopy. The isotacticity parameters of both polyacrylates were calculated from the ^{1}H n.m.r. spectra, giving the values $P_m = 0.44$ for poly(phenyl acrylate) and $P_m = 0.48$ for poly(4-fluorophenyl acrylate). The ^{13}C n.m.r. spectra recorded in deuterated benzene showed well-resolved signals for carbonyl carbon, methine carbon and methylene carbon. The assignments were made on the basis of Bernoullian statistics, with good agreement between the experimental and calculated values for both polyacrylates.

(Keywords: polyacrylates; microstructure; n.m.r.)

INTRODUCTION

Although poly(alkyl acrylate)s of high molecular weight have been analysed thoroughly by ^{1}H and ^{1}13C n.m.r. spectroscopy[1], the resolution of the spectra is much lower than that for poly(alkyl methacrylate)s and therefore the study of stereoregularity is more difficult. From the work reported by Matsuzaki and coworkers in the 1960s[2,3] and 1970s[4,5] it was clear that the functional groups of the poly(alkyl acrylate)s, i.e. methylene oxide, carbonyl carbon, etc., are not sensitive to the stereochemical configuration of the α-carbon of the main chain and only moderately accurate information can be derived from the analysis of the splitting of the α-CH and β-CH_2 resonances in the ^{1}H and ^{13}C n.m.r. spectra. More recently, we observed the insensitivity of the ester carbonyl carbon to the stereoregularity of methyl, ethyl and butyl polyacrylates prepared by free radical polymerization[6], but a clear splitting of the α-CH and β-CH_2 resonances gave enough information on the distribution of stereochemical sequences along the polymer chains. Suchoparek and Spevacek[7] have described recently in an interesting paper the stereochemical configuration parameters of poly(butyl acrylate)s prepared by group transfer polymerization and ionic polymerization through the use of modern two-dimensional techniques like homonuclear COSY and heteronuclear HETCOR correlations [8–10]. Although the decoupled ^{13}C n.m.r. spectrum registered using C_6D_6 as solvent gave carbonyl resonances which were split into several peaks, they centred their attention on the two-dimensional analysis of the relatively well-resolved α-CH and β-CH_2 resonances, concluding that the corresponding polymers are Bernoullian from a stereochemical point of view.

On the other hand, we have observed that the presence of aromatic side substituents instead of aliphatic residues in polyacrylic chains gives rise to a noticeable effect on the splitting of the n.m.r. signals of several acrylic systems. This is a consequence of the diamagnetic anisotropy of the aromatic rings on the neighbouring acrylic units[11,12]. To study in depth the effects of aromatic ester groups on the stereochemical distribution of monomeric sequences and the splitting of ^{1}H and ^{13}C n.m.r. signals we prepared several poly(aryl acrylate)s with different substituents in the aromatic ring. In this paper we present a study of the stereoregularity of poly(phenyl acrylate) (PPA) and poly(4-fluorophenyl acrylate) (PFA) prepared by free radical polymerization, and an analysis of the corresponding ^{1}H and ^{13}C n.m.r. spectra recorded in benzene-d_6

EXPERIMENTAL

Materials

Phenol (Fluka), 4-fluorophenol (Fluka) and acryloyl chloride (Fluka) were used without further purification. Toluene and benzene (Panreac) were purified by standard procedures. Azobisisobutyronitrile (AIBN) (Merck) was recrystallized from ethanol (melting point 104°C). 2,4-Dimethylglutaric acid (Fluka) and 2-chlor-

---

* To whom correspondence should be addressed

ophenol (Scharlau) were used as received without further purification.

Synthesis of monomers

Phenyl and 4-fluorophenyl acrylates were synthesized by reacting the corresponding phenol with acryloyl chloride in the presence of NaOH as reported in the literature[13]. Freshly distilled acryloyl chloride (40 mmol) was slowly added to the corresponding phenol (40 mmol) in toluene (50 ml) in the presence of NaOH (50%) (40 mmol) and a small amount of hydroquinone. The reaction was allowed to proceed for 3 h at room temperature. After separation the organic layer was dried ($MgSO_4$) and concentrated *in vacuo*, and finally distilled at reduced pressure. The boiling point of the phenyl derivative was 120°C (20 mmHg) and that of the 4-fluorophenyl derivative 45°C (0.75 mmHg).

An equimolecular mixture of the *meso* and racemic isomers of bis(*o*-chlorophenyl) 2,4-dimethylglutarate (CPDG) was prepared by condensation of 2,4-dimethylglutaric acid with *o*-chlorophenol (Ferosa) in a solution of dried toluene, using *p*-toluenesulfonic acid as catalyst. Other experimental details are given elsewhere[14]. Both diastereoisomers were isolated by repeated fractional crystallization in hot heptane. The values of the melting temperature and melting enthalpy were calculated by calorimetry, and they were 360 ∓ 1 K and 6.0 ∓ 1 Kcal mol^{-1}, respectively. The *meso*-CPDG is a liquid at room temperature and it does not crystallize at lower temperatures.

Polymerization

An appropriate quantity of the relevant monomer with benzene and AIBN in a standard reaction tube (100 ml) was degassed with O_2-free N_2. The tube was tightly sealed and then kept at 85°C. Polymerization was allowed to proceed for 3 h. The polymer was precipitated in excess methanol, filtered off, purified by reprecipitation from chloroform solution with methanol and finally dried in vacuum at 50°C.

Measurements

N.m.r. spectra of polymers were recorded using a Varian Unity-500 spectrometer operating at 499.8 MHz for ^1H n.m.r. experiments and 125.7 MHz for ^{13}C n.m.r. experiments. Spectra were recorded at 40°C in deuterated benzene solvent with tetramethylsilane as internal reference. F_1-decoupled COSY spectra were obtained for 2% PFA solutions using the pulse sequence RD-90°-$t_1/2$-180°-$(\Delta t_1/2)$-45°-FID. The fixed interval Δ was set at 0.175 s. A total of 32 scans with 640 increments were accumulated with a relaxation delay of 4 s. A sine-bell apodization function without phase shift was applied in both dimensions before Fourier transformation. The total acquisition time was 15 h. A classical $^{13}C-^1H$ HETCOR spectrum with proton decoupling in the F_1 domain was obtained for a 5% solution of PFA in C_6D_6. The delay time D_1 was set at 3.7 μs and the number of increments was 64. A sine-bell apodization function with phase shift was applied in both dimensions prior to Fourier transformation. The total acquisition time was 15 h.

Thermal analysis was carried out on a Perkin–Elmer DSC-2C instrument at a heating rate of 20 K min^{-1}. Weight and number average molecular weights ($\bar{M}_w$ and $\bar{M}_n$) were determined by gel permeation chromatography (g.p.c.) on a Waters 150-C. Four columns packed with microstyragel of pore sizes 500, 10^4, and 10^5 and 10^6 Å were used. The elution solvent was tetrahydrofuran (THF) and the flow rate was maintained at 1 ml min^{-1}. Calibration of g.p.c. results was carried out with standard polystyrene samples obtained from Waters. Weight average molecular weights, number average molecular weights and $\bar{M}_W/\bar{M}_n$ were calculated from g.p.c. chromatograms using the Mark–Houwink parameters $K = 1.6 \times 10^{-4}$ dl g^{-1} and $a = 0.706$ for polystyrene.

RESULTS AND DISCUSSION

PPA and PFA were synthesized by free radical polymerization in benzene solution at 85°C using AIBN as initiator . Relatively high conversions were reached in 3 h of reaction for both systems. *Table 1* shows the glass transition temperatures of these polymers and their molecular weight distributions. The value of T_g for PPA is in accordance with the values of T_g reported in the literature[15], being somewhat higher than that for PFA. It is noteworthy that PFA has a higher molecular weight and lower polydispersity ($\bar{M}_W/\bar{M}_n$) in comparison to PPA, although in both cases the parameters are in the range expected for classical free radical polymerization without noticeable transfer reactions. The difference in the molecular size parameters probably arises from the termination process (coupling or disproportionation) which gives rise to a broadening of the molecular weight distribution. In this sense, the data obtained seem to indicate that the disproportionation mechanism is favoured for the free radical polymerization synthesis of PFA.

Figure 1 shows parts of the high field 500 MHz ^1H n.m.r. spectra of PPA and PFA. Signals centred at 2.05 ppm are assigned to equivalent methylene protons in syndiotactic configurations, whereas signals centred at 1.9 and 2.38 ppm are assigned to non-equivalent methylene protons in isotactic configurations. The sharp peak at 2.90 ppm is assigned to the tertiary α-CH proton for both polymers. This assignment is supported by the COSY spectrum of PFA shown in *Figure 2* and is consistent with assignments suggested by Bovey[16,17] for low molecular weight models of polyacrylic chains as

Table 1 Values of the glass transition temperatures, number and weight average molecular weights and polydispersities of phenyl and 4-fluorophenyl polyacrylates synthesized in benzene at 85°C

Polymer	Conversion (% by weight)	T_g (K)	10^{-3} $\bar{M}_n$	10^{-3} $\bar{M}_W$	$\bar{M}_W/\bar{M}_n$
PPA	60.0	333	22	97	4.4
PFA	62.0	325	58	158	2.7

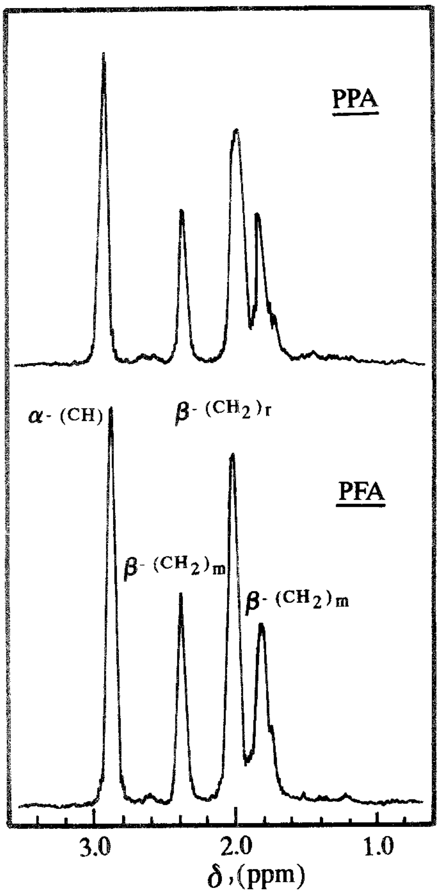

Figure 1 Parts of the 500 MHz ^{1}H n.m.r. spectra of PPA and PFA recorded in benzene-d$_6$ at 40°C

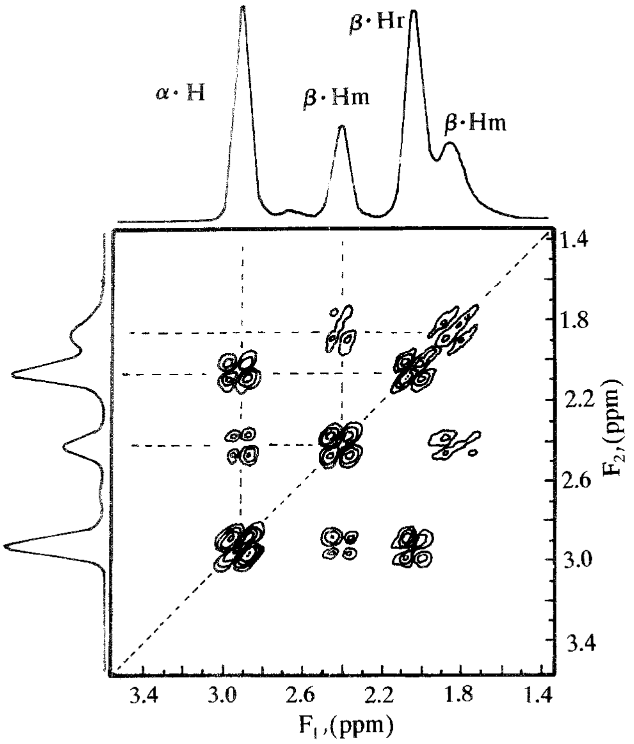

Figure 2 The 500 MHz two-dimensional homonuclear correlated (COSY) spectrum of PFA. The normal spectrum is along the diagonal and the cross-peaks connect protons which are j coupled

well as for several poly(alkyl acrylate)s. The COSY spectrum shows coupling between the non-equivalent methylene protons H_A and $H_{A'}$ and between these protons and the backbone methine proton H_X. In addition, the equivalent methylene protons H_A in the syndiotactic configuration appear to be coupled with the backbone methine proton H_X (*Figure 3*). On the other hand, the two-dimensional HMQC ^{13}C–^{1}H correlated maps of *Figure 4* show the correlations between the methine and methylene protons in the intervals 1.60–2.60 ppm (β-CH$_2$) and 2.80–3.10 ppm (α-CH) with the corresponding carbon atoms of the main acrylic chains of PPA and PFA. The most interesting conclusion from the analysis of these maps is that the contour of the signal assigned to the correlated β-CH$_2$ for racemic dyads indicates that the decoupled ^{13}C signal for this kind of dyad is shifted somewhat to lower field with respect to the ^{13}C signals of the β-CH$_2$ units for *meso* sequences.

According to the assignments of β-CH$_2$ and α-CH protons for m and r dyads of PPA and PFA, the propagation probabilities of m and r placements can be calculated from the ^{1}H n.m.r. spectra by comparison of the integrated intensities of the signals of methylene protons in m and r sequences. We obtained a value for the isotacticity probability (or isotacticity parameter) P_m of 0.44 for the free radical polymerization of phenyl acrylate, rather similar to that reported by Gueniffey and Pinazzi[18], and a value of 0.48 for the free radical polymerization of 4-fluorophenyl acrylate. The free radical polymerization of both monomers in the experimental conditions of this work can be considered Bernoullian from a stereochemical point of view. Values for P_m of 0.49, 0.42, 0.44 and 0.44 for the free radical polymerizations of methyl acrylate[2], isopropyl acrylate[4], ethyl acrylate and butyl acrylate[6], respectively, are described in the literature. More recently, Suchoparek and Spevacek[7] have reported a value for P_m of 0.49 for the group transfer polymerization of butyl acrylate in tetrahydrofuran at −10°C.

It is well known that ^{13}C n.m.r. spectroscopy provides accurate information on the stereochemical configu-

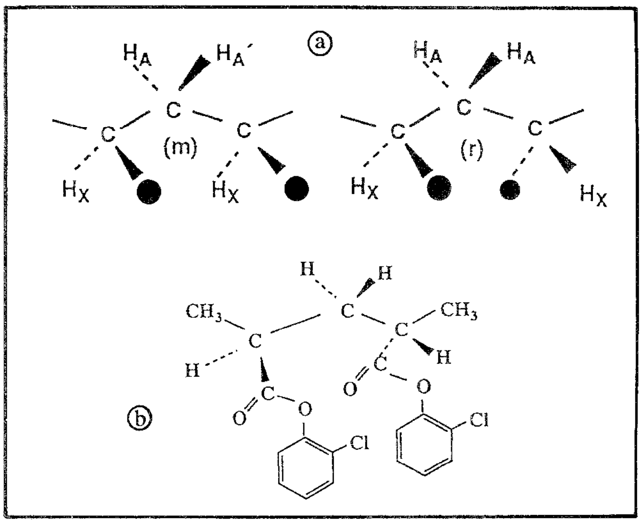

Figure 3 Schematic representation of the racemic and *meso* dyads of PPA and PFA (a) and the chemical structure of the model dimer CPDG(b)

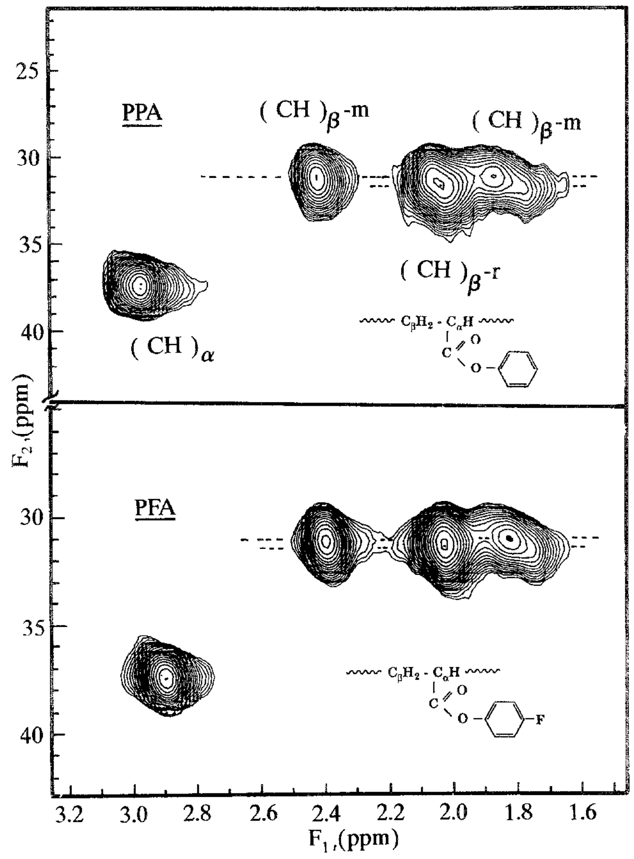

Figure 4 Two-dimensional HMQC $^{13}C-^{1}H$ correlated spectra of PPA and PFA

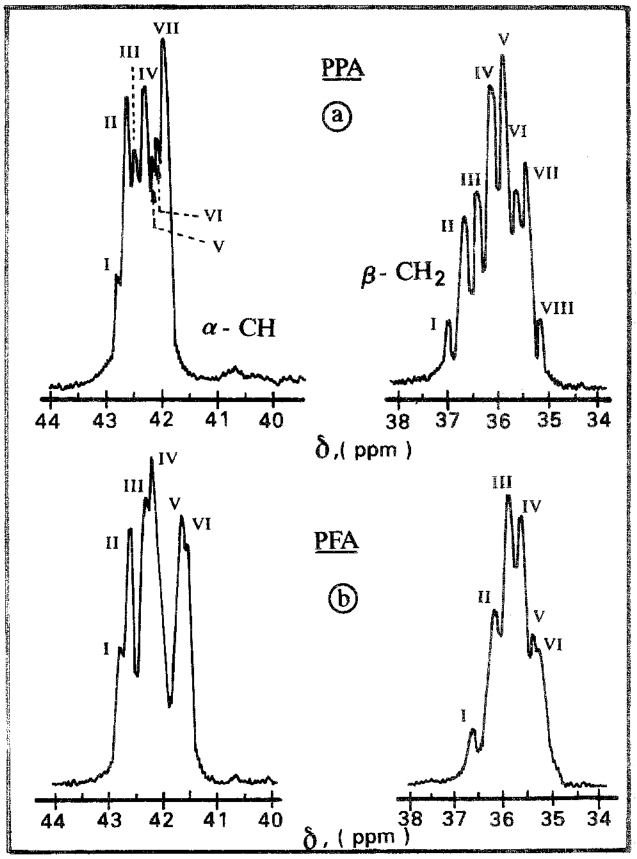

Figure 5 Enlarged ^{13}C n.m.r. signals of the methylene and methine carbon atoms of PPA (a) and PFA (b) recorded in benzene-d_6 at 40°C

rations of vinylic and acrylic polymer chains in terms of triads, tetrads or even longer sequences [9,10,18]. In this sense, we analysed the proton-decoupled ^{13}C n.m.r. spectra of PPA and PFA, using deuterated benzene as solvent. We have observed that the use of this solvent gives rise to a clearer resolution of n.m.r. signals, probably because of the diamagnetic effect of the ring current of the aromatic groups on the chemical shifts of the corresponding n.m.r. signals of the functional groups of the polyacrylates, i.e. α-CH, β-CH_2 and the aromatic ester group. *Figure 5* shows the enlarged ^{13}C n.m.r. signals of the β-CH_2 (34.5–38.0 ppm) and α-CH (41.0–43.5 ppm) carbon atoms of PPA (*Figure 5a*) and PFA (*Figure 5b*). The signals are split into different peaks assigned to the different stereochemical sequences in terms of triads for the α-CH signals and tetrads for the β-CH_2 signals. The assignments of individual peaks and the corresponding chemical shifts are collected in *Tables 2* and *3*. These assignments were made following a similar trend reported for poly(alkyl acrylate)s[5–7].

In order to prove the assignments of the signals to the stereochemical sequences given in *Tables 2* and *3*, we prepared a model compound which mimics the structure of the racemic and *meso* dyads of both PPA and PFA, namely bis(*o*-chlorophenyl) 2,4-dimethylglutarate (see *Figure 3b*). This compound was chosen because it is possible to isolate the *meso* and racemic stereoisomers by selective fractional crystallization under mild conditions from a mixture of both isomers[14]. This was not possible with the 4-halophenyl derivatives. Parts of the proton-decoupled ^{13}C n.m.r. spectra of the racemic and *meso*

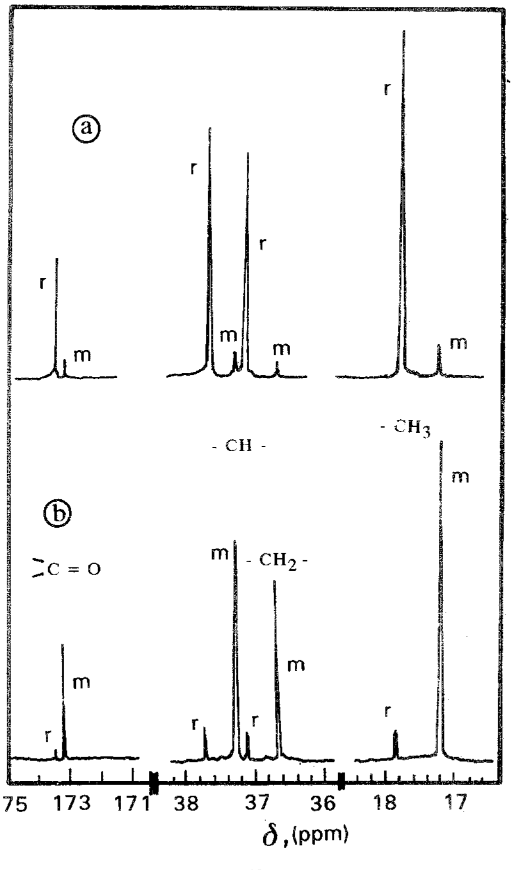

Figure 6 Parts of the decoupled ^{13}C n.m.r. spectra of the predominantly racemic (a) and *meso* (b) isomers of the model compound bis(*o*-chlorophenyl) 2,4-dimethylglutarate

Table 2 Assignments of the stereoregular sequence fractions of PPA prepared by free radical polymerization in benzene at 85°C

Carbon	Peak	Chemical shift (ppm)	Assignment	Molar fractions	
				Experimental[a]	Calculated[b]
Cβ	I	36.70		0.04_1	
	II	36.40	rrr + rmr	0.11_2	0.314
	III	36.15		0.13_2	
	IV	35.90	mmr	0.21_2	0.271
	V	35.60	rrm	0.27_2	0.276
	VI	35.40		0.08_1	
	VII	35.20	mmm + mrm	0.12_9	0.193
	VIII	34.95		0.02_0	
Cα	I	42.45		0.06_0	
	II	42.40	rr	0.21_3	0.314
	III	42.25		0.11_3	
	IV	42.05	mr	0.26_1	0.490
	V	41.90		0.05_4	
	VI	41.85		0.05_8	
	VII	41.70	mm	0.20_4	0.190
CO	I	173.46	mrrm	0.05_3	0.061
	II	173.42	mrrr + rrrr	0.24_3	0.253
	III	173.24	rmrr	0.12_8	0.154
	IV	173.16	mmrr	0.25_8	0.243
	V	173.06	mmrm	0.11_0	0.095
	VI	172.94	rmmr	0.05_8	0.061
	VII	172.82	mmmr	0.12_0	0.095
	VIII	172.68	mmmm	0.03_0	0.037

[a] From the spectrum measured in deuterated benzene
[b] Calculated by assuming Bernoullian statistics ($P_m = 0.44$ for PPA)

Table 3 Assignments of the stereoregular sequence fractions of PFA prepared by free radical polymerization in benzene at 85°C

Carbon	Peak	Chemical shift (ppm)	Assignment	Molar fractions	
				Experimental[a]	Calculated[b]
Cβ	I	37.20		0.05_3	
	II	36.70	rrr + rmr	0.19_3	0.260
	III	36.50	mmr	0.26_7	0.255
	IV	36.20	mrr	0.23_6	0.244
	V	35.90	mmm + mrm	0.25_1	0.240
Cα	I	43.25			
	II	43.10	rr	0.25_2	0.260
	III	42.90			
	IV	42.80	mr	0.481	0.499
	V	42.20			
	VI	42.10	mm	0.26_6	0.240
CO	I	174.25	mrrm	0.05_9	0.063
	II	174.15	mrrr + rrrr	0.18_0	0.197
	III	174.00	rmrr	0.11_8	0.120
	IV	173.85	mmrr	0.26_1	0.245
	V	173.75	mmrm	0.13_3	0.120
	VI	173.50	mmmr + rmmr	0.17_4	0.182
	VII	173.40	mmmm	0.07_4	0.058

[a] From the spectrum measured in deuterated benzene
[b] Calculated by assuming Bernoullian statistics ($P_m = 0.48$ for PFA)

isomers are shown in *Figures 6a* and *6b*, respectively. It is clear from these spectra that the racemic isomer presents signals at lower field than does the corresponding *meso* isomer, which supports the assignments suggested for the α-CH and β-CH_2 resonances of PPA and PFA according to the stereochemical sequences collected in *Tables 2* and *3*.

Figures 7a and *7b* show the patterns of signals assigned to the ester carbonyl groups. It is noteworthy that this group is not very sensitive to the stereoregularity in poly(alkyl acrylate)s, but we have obtained excellent resolution of the signals in terms of stereochemical pentads. This phenomenon probably arises from the specific diamagnetic effect of the aromatic ring on the neighbouring ester carbonyl group. The assignments of individual peaks and the corresponding chemical shifts are collected in *Tables 2* and *3*. The last two columns of these tables show the molar fractions of tetrad and pentad stereosequences determined experimentally from the signals in the spectra and those calculated from Bernoullian statistics for the addition of monomeric units to growing free radical chains with the isotacticity parameters $P_m = 0.44$ and $P_m = 0.48$ determined from the ^1H n.m.r. spectra for PPA and PFA, respectively. The agreement between the experimental and calculated parameters indicates that the assignments are correct and supports the use of Bernoullian statistics for the

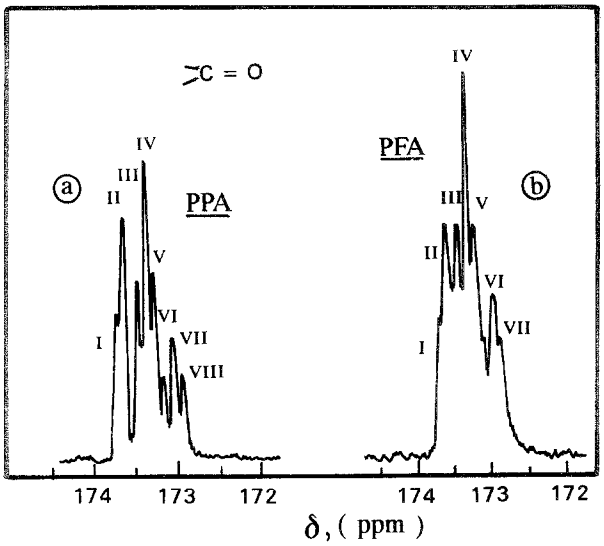

Figure 7 Expanded ^{13}C n.m.r. signals of the ester carbonyl groups of PPA (a) and PFA (b) recorded in benzene-d_6 at 40°C

propagation step of the free radical polymerization of these acrylic monomers. In addition, the sensitivity of the functional groups to the stereochemical configurations of the monomeric sequences in the presence of aromatic side substituents is clearly demonstrated.

ACKNOWLEDGEMENTS

We thank the Diputacion Foral de Guipuzcoa and CICYT (MAT 93-0749-C03-01) for supporting this work.

REFERENCES

1 Pham, Q. T., Petiaud, R. and Waton, H. 'Proton and Carbon NMR Spectra of Polymers', Penton Press, London, 1991
2 Matsuzaki, K., Uryu, T., Ishida, A., Ohki, T. and Takeuchi, M. *J. Polym. Sci. A-1* 1967, **5**, 2167
3 Matsuzaki, K., Uryu, T., Ishida, A and Takeuchi, M. *J. Polym. Sci. C* 1967, 2099
4 Matsuzaki, K., Okada, M. and Hosonuma, K. *J. Polym. Sci. A-1* 1972, **10**, 1179
5 Matsuzaki, K., Kanai, T., Kawamura, T., Matsumoto, S. and Uryu, T. *J. Polym. Sci., Polym. Chem. Edn.* 1973, **11**, 961
6 Goñi, I., Gurruchaga, M., Valero, M. and Guzman, G. M. *Polymer* 1993, **34**, 178
7 Suchoparek, M. and Spevacek, J. *Macromolecules* 1993, **26**, 102
8 Derome, A., 'Modern NMR Techniques for Chemistry Research', Pergamon Press, Oxford, 1987
9 Ibbett, R. N. 'NMR Spectroscopy of Polymers' Blackie, London, 1993
10 Koenig, J. L. 'Spectroscopy of Polymers', ACS, Washington, DC, 1992
11 San Roman, J., Madruga, E. L. and Del Puerto, M. A. *Angew. Makromol. Chem.* 1979, **78**, 129
12 San Roman, J. and Madruga, E. L. *Eur. Polym. J.* 1982, **18**, 481
13 Chao, H. S. -I., Hovatter, T. W. and Johnson, B. C. *J. Polym. Sci. Polym. Chem. Edn.* 1989, **27**, 3371
14 San Roman J., Riande, E., Madruga, E. L. and Saiz, E. *Macromolecules* 1990, **23**, 1923
15 Pizzirani, G., Magagnini, P. and Giusti, P. *J. Polym. Sci. A-2* 1971, **9**, 1133
16 Bovey, F. A. *Makromol. Chem. Macromol. Symp.* 1988, **20/21**, 105
17 Bovey, F. A. 'Chain Structure and Conformation of Macromolecules', Academic Press, New York, 1982
18 Gueniffey, H. and Pinazzi, C. P. *Makromol. Chem.* 1971, **148**, 93