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Determination of the Microstructure of Poly(methyl α-fluoroacrylate) by NMR Spectroscopy

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Summary

The 300 MHz pmr, 282 MHz fmr and 20 MHz cmr spectra of poly(methyl α-fluoroacrylate) that was prepared by free radical initiated polymerization have been recorded. They indicate the polymer to have a Bernoullian distribution of stereosequences, with $\sigma = P(m) = 0.41$. Pentad stereosequence distributions were measurable from the 282 MHz fmr spectra of this polymer, but only dyad and triad distributions could be determined from the pmr and cmr spectra, respectively.

Introduction

The sterochemical structures of polymers prepared from acrylates and α-substituted acrylates by anionic polymerization methods have been investigated extensively [YUKI and HATADA 1979]. The microstructures of such polymers prepared by free radical methods have also been investigated, but to a lesser extent, partly due to the non-polymerizability at 60°C of many of the monomers [CHIKANISHI and TSURUTA 1965]. Although the stereochemical structures of polymers derived from α-chloroacrylates [MATSUZAKI et al. 1969, DEVER et al. 1975] and α-bromoacrylates [SAUNDERS 1979] have been investigated, no information is available concerning polymers derived from α-fluoroacrylates. It was felt that such information would contribute to our understanding of the influence of α-substituents on the stereochemistry of α-substituted acrylate polymerizations, since polar and steric effects are considered to be involved. Accordingly, this paper describes the microstructure of poly(methyl α-fluoroacrylate) as determined by pmr, cmr and fmr spectroscopy.

Results and Discussion

Methyl α-fluoroacrylate was prepared by the following sequence of reactions, details of which will be

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published subsequently.

$$CH_2{=}CHCOOCH_3 \xrightarrow{Br_2} BrCH_2\text{-}CHBrCOOCH_3 \xrightarrow[90°/8\ mm\ Hg]{quinoline}$$

$$CH_2{=}CHBrCOOCH_3 \xrightarrow{Br_2} BrCH_2\text{-}CHBr_2COOCH_3 \xrightarrow[140\text{-}160°/32\ mm\ Hg]{SbF_3/SbCl_5}$$

$$BrCH_2CBrFCOOCH_3 \xrightarrow[\phi_2O]{Zn/Thiourea} CH_2{=}CFCOOCH_3$$

The pmr spectrum of the monomer was identical to that described by PITTMAN et al. (1980) and glc examination of the monomer indicated it was free of impurities.

The monomer was polymerized in bulk at 60°C using AIBN as initiator and was purified by twice reprecipitation from chloroform solution into methanol.

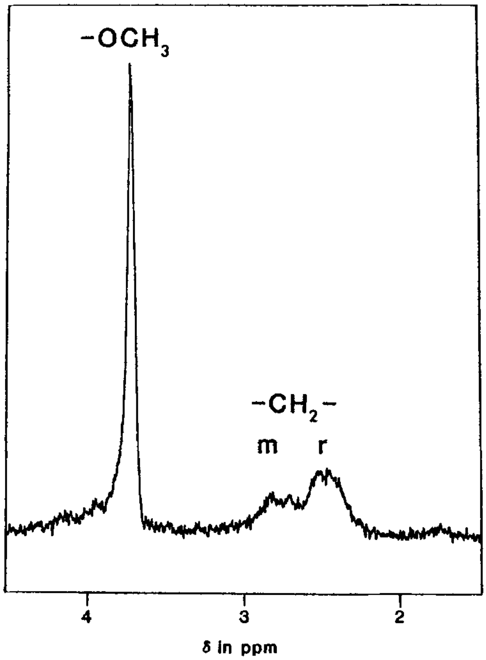


Figure 1. 300 MHz pmr Spectrum of Poly(methyl α-fluoroacrylate) in $CDCl_3$ Solution at 55°C.

Figure 1 shows the 300 MHz pmr spectrum of the polymer in $CDCl_3$ solution at 55°C. The methylene proton resonance is observed in two partially resolved areas that are tentatively assigned to meso-(δ=2.6 - 3.0 ppm) and racemic-(δ=2.2 - 2.6 ppm) configurations. Based on the relative amounts of these resonances, the meso content, P(m), of the polymers is estimated to be 0.4. The methoxy proton resonance of this polymer is observed as a singlet, even when the polymer is dissolved in an aromatic solvent (2,4-dinitrofluorobenzene) at high temperature (120°C), in contrast to the behavior of many other polymers derived from α-substituted acrylates.

Figure 2 shows the 20 MHz cmr spectrum of poly(methyl α-fluoroacrylate) in $CDCl_3$ solution at room temperature. Due to C-F couplings, double signals are observed for the carbonyl (δ=∿170 ppm; J_{C-F}=25 Hz) and α-carbon (δ=∿92 ppm; J_{C-F}=193 Hz) resonances.

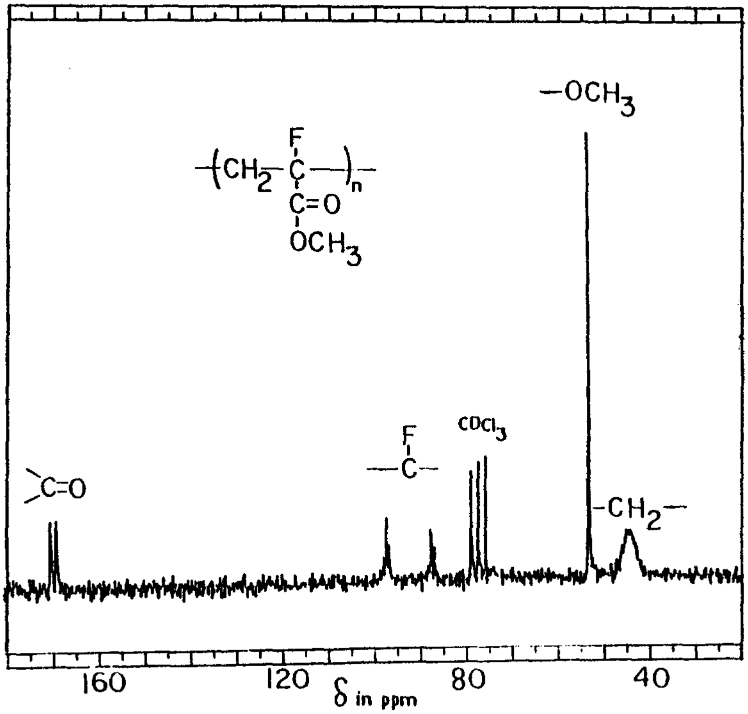


Figure 2. 20 MHz cmr Spectrum of Poly(methyl α-fluoroacrylate) in $CDCl_3$ Solution at Room Temperature.

The latter consist of three peak patterns that are assigned to mm-, (mr+rm)- and rr-stereosequences in order of increasing field and are of relative area 0.16, 0.47 and 0.37, respectively. These areas correspond well to those calculated (0.16, 0.48 and 0.36) for a Bernoullian polymer, when P(m) = 0.40. The carbonyl carbon resonances also contain stereosequence information but the individual signals have very similar chemical shifts and are not well resolved.

Figure 3 shows the 282 MHz fmr spectrum of poly(methyl α-fluoroacrylate) in $CDCl_3$ solution at 55°. Nine resonances are evident, indicating that pentad stereosequences are being observed. The relative intensities of these resonances, their assignments and calculated resonance intensities based on these assignments, assuming the polymer has a Bernoullian distribution of stereosequences with P(m) = 0.41, are given in Table I. The chemical shifts listed in Table I are expressed in ppm upfield from $CFCl_3$, as described elsewhere [MAJUMDAR and HARWOOD 1981].

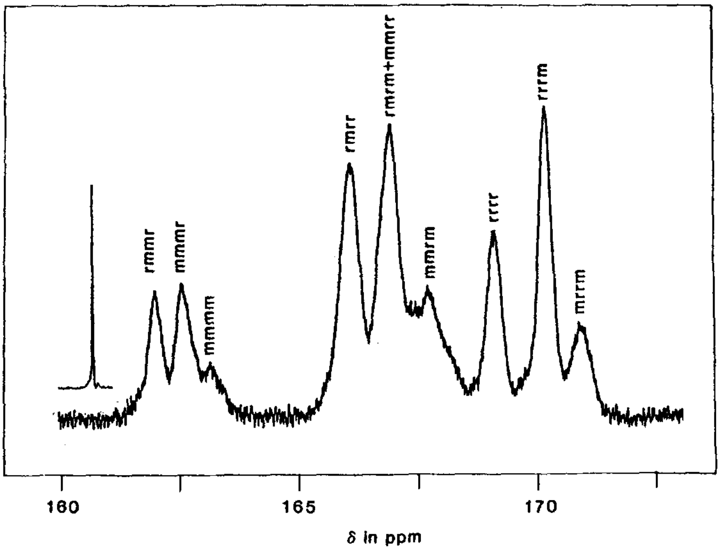


Figure 3. 282 MHz fmr Spectrum of Poly(methyl α-fluoroacrylate) in $CDCl_3$ Solution at 55°C.

Thus, the pmr, cmr and fmr spectra of poly(methyl α-fluoroacrylate) indicate it to have a Bernoullian stereosequence distribution with P(m) = 0.41. Our data are also consistent with a P(m) value of 0.59, but this alternative seems less likely since free radical initiated polymerizations of most substituted acrylate esters yield either atactic or slightly syndiotactic polymers. Definite assignments could be made if isotactic or syndiotactic poly(methyl α-fluoroacrylate) could be prepared.

TABLE I

Intensities and Assignments of ^{19}F Resonances of Radically Prepared Poly(Methyl α-Fluoroacrylate)

PENTAD	CHEMICAL SHIFT, ppm	RESONANCE AREA	
		EXPERIMENTAL	CALCULATED*
rmmr	162.1	0.06	0.059
mmmr	162.6	0.07	0.081
mmmm	163.2	0.03	0.028
rmrr	166.1	0.17	0.168
rmrm+mmrr	167.0	0.24	0.234
mmrm	167.8	0.09	0.081
rrrr	169.2	0.11	0.121
rrrm	170.3	0.17	0.168
mrrm	171.0	0.06	0.059

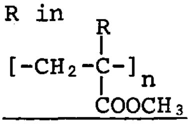
*Bernoullian distribution with P(m) = 0.41

Table II compares P(m) values reported for a number of polymers derived by free radical initiated polymerization from methyl α-substituted acrylates. Based on steric substituent constants that have been evaluated [TAFT 1956] for the various R groups listed in Table II the substituents may be arranged in the following order of increasing steric requirements: $H<F<Cl< Br \sim CH_3 <C_6H_5$. Considering the first five entries in Table II, the P(m) values generally decrease as the steric requirements of R increase, but the P(m) values observed for the cases where R is C_6H_5 or $-CH_2OC_6H_5$ are much higher than they should be, based on a consideration of steric effects alone. It

is clear that much more data must be accumulated before a complete understanding of the influence of monomer structure on the stereochemistry of these polymerizations emerges.

TABLE II

P(m) Values Observed for Poly(methyl α-substituted acrylates) Prepared by Free Radical Initiated Polymerization

R in  $[-CH_2-\overset{R}{\underset{COOCH_3}{C}}-]_n$	Polymerization Conditions	P(m)	Reference
H	toluene, AIBN, 60°C	0.47	SUZUKI, et al. 1974
F	bulk, AIBN, 60°C	0.41	This work
Cl	toluene, benzoyl peroxide, 70°C	0.28	DEVER, et al. 1975
Br	toluene, decanoyl peroxide, 50°C	0.32	SAUNDERS, 1979
CH_3	bulk, AIBN, 60°C	0.21	SUZUKI and HARWOOD, 1975
C_6H_5	toluene, AIBN, 60°C	0.50	YUKI, et al. 1971
$CH_2OC_6H_5$	toluene, AIBN, 60°C	0.48	LENZ, et al. 1979

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