¹³C NMR Characterization of Polymers from 2,2,2-Trifluoroethyl Methacrylate

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ABSTRACT: In an attempt to develop structural characterisation of polymers from fluorinated acrylic derivatives, a detailed ¹³C NMR analysis of free radical and anionic poly(2,2,2-trifluoroethyl methacrylate) (poly(TFEM)) was performed as compared to relevant literature studies concerning the corresponding methyl methacrylate (MMA) polymers. On the other side, the moderately syndiotactic microstructure of the poly(TFEM) samples fits very well with that of corresponding poly(MMA) samples and can be interpreted on the basis of the same statistical distribution of triads. Thus it appears that the presence of the —CH₂—CF₃ group does not affect in a determining way the stereochemistry of the polymerization. According to this final statement, anionic initiators give prevalently isotactic poly(TFEM) as detected by ¹³C NMR.

KEY WORDS NMR-Spectroscopy / Polymer Stereochemistry / Poly(2,2,2-trifluoroethyl methacrylate) / Methacrylate Polymers / Fluoro Containing Macromolecules /

Polymers of fluorinated acrylic derivatives have acquired an increasing interest for high performance coating applications. Indeed these materials combine the good film-forming characteristics of acrylic polymers, with excellent optical properties, improved outdoor stability,^{1–4} low refractive index and surface tension.⁵ In particular they are used for several advanced applications as clad for optical fibers,⁶ in microlithography,⁷ as heat-resistant optical materials,⁸ for protecting surfaces particularly against humidity⁹ and so on.¹⁰ The rapid development arising from the above interest was not flanked by an adequate fundamental characterization as far as NMR studies are concerned. Indeed there are only few reports concerning ¹H, ¹³C, and ¹⁹F NMR data of poly(methyl α-fluoroacrylate)^{1,11} and

¹H NMR spectra of 2,2,2-trifluoroethyl methacrylate^{12–13}; recently the ¹⁹F NMR spectra of some poly(fluoroalkyl α-fluoroacrylate)s were also reported.¹⁴ In order to contribute further this last aspect we report here about a detailed investigation by ¹³C NMR of poly(2,2,2-trifluoroethyl methacrylate) [poly(TFEM)] samples prepared by free radical and anionic initiators. This work had the two-fold objective of correlating spectral features with structural aspects and to check possible effects of the —CF₃ group in the side chain on polymerization stereochemistry.

EXPERIMENTAL

The free radical polymer of TFEM was obtained by polymerization at 65°C in dioxane

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(50 ml), using 10 g of monomer and 0.4 g of α, α' -azobisisobutyronitrile (AIBN) as initiator. The reaction was carried out for 132 h. The polymer was isolated by precipitation with *n*-hexane.

1 g of monomer, 5 ml of toluene, and 10 mg of lithium *tert*-butoxide as initiator were used for the anionic polymerization of the TFEM. The reaction was carried out at -20°C for 7 days. The polymer was isolated from the polymerization mixture by precipitation with benzene. ^{13}C NMR spectra were obtained at 25°C on CDCl_3 solutions using 5 mm inner diameter tubes. A Varian Gemini 200 spectrometer (50.3 MHz ^{13}C , pulse angle 70° , acquisition time 0.4 s, interval between pulses 2 s, spectral width 15000 Hz, number of scans 45000 and 67000) was used under conditions of full proton decoupling. Chemical shifts were measured with respect to the resonance of CDCl_3 , which was taken as 77.0 ppm downfield from tetramethylsilane (TMS).

RESULTS AND DISCUSSION

^{13}C NMR Features of Free Radical Poly-(TFEM)

The spectrum (Figure 1) is characterized by a good resolution, each of the six C-atoms of the monomeric units showing resonances in well-separated spectral range. The chemical shifts of $(\text{CH}_3)\alpha$, $\text{C}\alpha$, CH_2 (backbone), and also $\text{C}=\text{O}$ are very close to those of free radical poly(methyl methacrylate) [Poly(MMA)], while the CF_3 is effective on the resonance of the carbon in the $\text{O}-\text{CH}_2$ group which is shifted to lower field (Table I).

The triads concentration for syndiotactic (*rr*), heterotactic (*mr*), and isotactic (*mm*) sequences can be evaluated by numerical integration of the resonances lines from $(\text{CH}_3)\alpha$, $\text{C}\alpha$, and $\text{C}=\text{O}$. The resulting values are very close to those observed for poly-(MMA) prepared under the same conditions (Table II). Indeed both polymers are mainly syndiotactic (about 56% *rr* triads). By using $\text{C}\alpha$ signals it is possible to calculate some

Figure 1. ^{13}C NMR spectrum of free radical poly(2,2,2-trifluoroethyl methacrylate).

Table I. Assignment of chemical shifts in ^{13}C NMR spectra of poly(TFEM) with reference to poly(MMA)

Spectral range	Chemical shift	Assignment	
	ppm	poly(TFEM)	Poly(MMA)
I	16–22	$(\text{CH}_3)\alpha$	$(\text{CH}_3)\alpha$
II	44–46	$\text{C}\alpha$	$\text{C}\alpha$
III	50–56	CH_2	$\text{CH}_2, \text{OCH}_3$
IV	59–63	OCH_2CF_3	—
V	114–132	CF_3	—
VI	174–179	$\text{C}=\text{O}$	$\text{C}=\text{O}$

statistical parameters for the two polymers. For both polymers microtacticity sequences can be equally well interpreted by a Bernoullian or a 1st order Markov chain statistics model. It is of interest to note that the tacticity of poly(MMA) prepared at 135°C can be described by a Bernoullian statistics, while below 5°C the Markov 1st order model fits better the experimental results. In between 135°C and 5°C the tacticity distribution seems to be intermediate.¹⁵ This was confirmed by studying Poly(MMA) prepared by AIBN initiator at 60°C .^{16–17}

In case of the $\text{C}=\text{O}$ (Figure 2) pentads

Table II. Relative concentration of stereochemical triads in free radical poly(TFEM) and poly(MMA)

Triads	Poly(TFEM)				Poly(MMA)			
	$(\text{CH}_3)\alpha$	$\text{C}\alpha$	$\text{C}=\text{O}$	Average	$(\text{CH}_3)\alpha$	$\text{C}\alpha$	$\text{C}=\text{O}$	Average
<i>rr</i>	0.54	0.55	0.58	0.56	0.55	0.58	0.58	0.57
<i>mr</i>	0.41	0.38	0.38	0.39	0.39	0.37	0.37	0.38
<i>mm</i>	0.05	0.06	0.04	0.05	0.05	0.05	0.04	0.05

Figure 2. Expansion of the carbonyl region of ^{13}C NMR spectrum of free radical poly(TFEM).

Table III. ^{13}C NMR chemical shift and related assignment of resonance in free radical poly(TFEM)

	Chemical shift (ppm)	Assignment	Relative concentration		
			Experimental ^a	Calculated	
				b	c
(CH ₃) α	16.90	<i>rr</i>	0.54	0.56	0.55
	18.62	<i>mr</i>	0.41	0.37	0.38
	21.08	<i>mm</i>	0.05	0.06	0.06
	44.77	<i>rr</i>	0.55	0.56	0.55
C α	44.94	<i>rmrr</i>		0.21	0.22
	45.03	<i>mr</i> <i>rmrm</i>	0.38	0.07	0.07
	45.06	<i>mmrr</i>		0.07	0.07
		<i>mmrm</i>		0.02	0.02
	45.57	<i>mm</i>	0.06	0.06	0.06
		<i>rr</i>			
CH ₂	50–56	<i>mr</i> <i>mm</i>			
CH ₂ –CF ₃	61.14		$J_{\text{C-F}} = 37 \text{ Hz}$		
CF ₃	122.83	<i>rr</i>	$J_{\text{C-F}} = 276 \text{ Hz}$		
	122.92	<i>mr</i>			
		<i>mm</i>			
C=O	174.13			0.04	0.04
	174.33	<i>mm</i> <i>mmmr</i>	0.04	0.02	0.02
	174.37	<i>mmmm</i>		0.00	0.00
	174.51	<i>rmrr</i>		0.21	0.22
	174.57	<i>mmrr</i>		0.07	0.07
	174.82	<i>mr</i> <i>rmrm</i>	0.38	0.07	0.07
	174.86	<i>mmrm</i>		0.02	0.02
	175.13	<i>mrrrrm</i>		0.02	
	175.20	<i>rrrr</i> <i>rrrrrr</i>	0.3	0.18	0.32
	175.24	<i>mrrrr</i>		0.12	
	175.44	<i>rmrrrm</i>		0.04	
	175.51	<i>mrrr</i> <i>rmrrrr</i>	0.22	0.12	0.22
		<i>mmrrrm</i>		0.01	
	175.54	<i>mmrrrr</i>		0.04	
	175.87	<i>rmrrmr</i>		0.02	
	175.99	<i>mrrm</i> <i>mmrrmr</i>	0.05	0.01	0.04
	176.06	<i>mmrrmm</i>		0.00	

^a Determinated on the basis of corresponding peaks areas in the ^{13}C NMR spectra.^b From Bernoullian statistics ($P_m = 0.25$).^c From 1st order Markov chain statistics with the parameters of Table III.

concentrations (Table III) are also very similar for the two polymers confirming that the free radical propagation stereochemistry is substantially the same with $-\text{COOCH}_3$ or $-\text{COOCH}_2\text{CF}_3$ side chains. The resolution achieved in the carbonyl region of the ^{13}C NMR spectrum of radical poly(TFEM) (Figure 2) allows assignment of each peak to

the *rr*-centred related heptads (Table III) again with reference to poly(MMA).^{16,17}

In any case the close similarity between TFEM and MMA polymerization stereochemistry during free radical chain propagation suggests similar interactions between incoming monomer and last inserted monomeric unit side chains. This would imply that

Figure 3. Expansion of range I ($(\text{CH}_3)_\alpha$) and II (C_α) of ^{13}C NMR spectra of the poly(TFEM): a) anionic; b) radical.

the replacement of a H-atom of MMA with a CF_3 group in TFEM does not seem to affect these interactions in spite the change of polarity involved.

^{13}C NMR Features of Anionic Poly(TFEMA)

The same groups of signals as in the radical poly(TFEM) spectrum was observed for the anionic polymer, but the relative intensities of each group were different. Figure 3 shows the spectrum expansion of the ranges I and II ($(\text{CH}_3)_\alpha$ and C_α , respectively) (Table I) for both polymers. The expansion of the carbonyl region shows three groups of signals, but in this case only the triad assignment was possible.

The anionic polymerization of methacrylates can give polymers with a wide range of stereoregularity.¹⁸ The utilization of the lithium tertiary alkoxides such as lithium *tert*-butoxide as initiator and nonpolar solvents gives highly isotactic polymers.¹⁹ The moderate isotacticity of the present sample is reported with the fact that it was possible to examine only the chloroform soluble fraction. The

insoluble material can be expected to be much more isotactic. In any case the differences observed were large enough, confirming a similar assignment as for poly(MMA). Accordingly the comparison of the spectra suggests that the anionic polymer is predominantly isotactic ($mm=0.590$, $mr=0.258$, $rr=0.152$, $P_m=0.768$, and $P_r=0.391$).

It is of interest to note that isotactic mechanism had been proposed for the anionic polymerization of TFEM in the presence of $\text{Li Zn C}_4\text{H}_9(\text{C}_2\text{H}_5)_2$ on the basis of the narrower peaks related to α -methyl protons even if it was stated¹² that the ^1H NMR spectra of the polymers prepared by anionic or free radical initiators are almost identical. In this connection ^{13}C NMR is much more effective for detecting stereochemical differences.

CONCLUDING REMARKS

^{13}C NMR investigation of free radical and anionic polymers from 2,2,2-trifluoroethyl metacrylate was carried out. The presence of

fluorinated methyl in the side chains provides fully resolved spectra, all the five C-atoms of the monomeric units giving characteristic resonance in well separated spectral regions allowing assignment of triads peaks for $(\text{CH}_3)\alpha$ and $\text{C}\alpha$ carbons, and up to heptads for the carbonyl carbons. The relative concentrations of the different microtacticity sequences of the free radical polymer are very similar to those of poly(MMA) and can be adequately described with bernoullian statistics ($P_m=0.25$, $P_r=0.75$) even if it is of interest to note that the stereochemical distribution can be also described with a first order Markow ($P_{m/m}=0.248$, $P_{r/r}=0.752$) statistics. The polymer obtained by anionic polymerization by lithium *tert*-butoxide in hydrocarbon solvent shows as detectable from ^{13}C NMR spectrum a substantial increase of tacticity with respect to the free radical sample. The comparison with poly(MMA) samples and the initiator used suggest that this anionic polymers is mainly isotactic thus confirming the same stereochemical behavior as for methyl methacrylate even with this last propagation mechanism.

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