Polymer Bulletin 48, 59-66 (2002)

Polymer Bulletin

Synthesis, characterization and thermal behavior of Poly(methyl-*n*-octadecyl itaconate) a comb-like polymer with crystallizable side chain

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Received: 12 September 2001/Revised version: 3 January 2002/Accepted: 10 January 2002

Abstract

The radical polymerization of methyl *n*-octadecyl itaconate initiated with AIBN, produces poly(methyl *n*-octadecyl itaconate) with a yield of 47% and a molecular weight of about 10^5 g/mol. ^{13}C-NMR studies point out that this polymer is mainly syndiotactic. The combined studies of DSC and solid state ^{13}C CP/MAS NMR indicate that the polymer side chains are able to crystallize in a paraffinic phase, presumably in an hexagonal form which melts at 44°C with a ΔH of 4.8Kcal/mol.

Introduction

Poly(itaconate)s have been extensively studied for many years [1,2]. Several of these works were oriented to the study of solid-state and solution properties [3-7] and more recently have increased the interest in the study of the thermal degradation of these materials [8,9]. On the other hand, tacticity of poly(itaconic acid) benzyl esters [10] and the effect of the polymerization temperature on the microstructure of the poly(di-*n*-butyl itaconate) have been investigated by ^{13}C NMR spectroscopy [11]. These reports point out that diesters are mainly syndiotactic, whereas the poly(mono itaconate) results in to fully atactic polymer.

Up to where we have knowledge, any report about preparation of poly mono and poly(methyl itaconate)s with long *n*-alkyl side chains (n>12) have been published. Poly(diitaconate) derivatives with long *n*-alkyl side chain have been prepared and some investigations were focussed on the study of solution properties [7], as well as its crystallizability [12, 13]. For derivatives with side chain lengths from 12 to 20 carbon atoms the side chains are able to crystallize displaying an increase in the melting temperature and fusion enthalpy with the side chain length [12, 13].

In this work we report on the synthesis and characterization of the poly(methyl *n*-octadecyl itaconate) and a study of the thermal behavior of this polymer using DSC and solid state ^{13}C NMR.

Experimental

Preparation of monomer and polymer.

Mono-*n*-octadecyl itaconate (MI-18) was obtained by esterification of itaconic acid with *n*-octadecyl alcohol 1:3 (mol:mol) using acetyl chloride as catalyst according to a general method previously reported by León *et al* for mono-*n*-alkyl itaconates with short alkyl side chains [5]. The ester was isolated and purified by dissolving the reaction mixture in hot *n*-heptane and allowing to crystallize at 30°C. Monoitaconate, a white powder, was recrystallized several times in the same solvent until no traces of alcohol were detected by TLC. Yield 41% m.p. 88-90°C. ^{1}H NMR (in $CDCl_3$) (ppm): 6.48 (s, 1H, $C\mathbf{H}_2{=}C$); 5.85 (s, 1H, $C\mathbf{H}_2{=}C$); 4,12 (t, 2H, $COC\mathbf{H}_2$); 3,36 (s, 2H, $CC\mathbf{H}_2CO$); 1.63 (m, 2H, $COOCH_2C\mathbf{H}_2$); 1.32 (br s, 30H, $COOCH_2CH_2(C\mathbf{H}_2)_{15}CH_3$); 0.90 (t, 3H, $C\mathbf{H}_3$). ^{13}C RMN (in $CDCl_3$) (ppm): 171.12; 167.03; 134.22; 128.73; 65.49; 52.46; 38.17; 32.32; 30.09; 29.97; 29.92; 29.76; 29.63; 28.92; 26.22; 23.08; 14,50.

Methyl-*n*-octadecyl itaconate (MeI-18) was prepared by methylation of monoester dissolved in cold methanol with an ethereal solution of diazometane [14,15]. Solvent was removed by evaporation and the residual mixture was dissolved in hot hexane, treated with magnesium sulfate and filtered. Hexane was removed by evaporation and the product was redisolved in hot methanol and allowed to crystallize at 5°C. The purity of the white solid powder monomer was confirmed by TLC. Yield 73%, m.p. 42-44°C. IR spectrum shows the lack of the carboxylic band at 3500cm^{-1}. ^{1}H RMN (in $CDCl_3$) (ppm): 6.31 (s, 1H, $C\mathbf{H}_2{=}C$); 5.69 (s, 1H,

$C\mathbf{H}_2$=C); 4.07 (t, 2H, $COC\mathbf{H}_2$); 3.75 (s, 3H, $OC\mathbf{H}_3$); 3.32 (s, 2H, $CC\mathbf{H}_2CO$); 1.63 (m, 2H, $COOCH_2C\mathbf{H}_2$); 1.26 (br s, 30H, $CH_2CH_2(C\mathbf{H}_2)_{15}CH_3$); 0.87 (t, 3H, $C\mathbf{H}_3$). Poly(methyl-*n*-octadecyl itaconate) (PMeI-18) was prepared by bulk polymerization at 60°C during 48 hours under a nitrogen atmosphere using AIBN (1%) as initiator. The polymer obtained was then dissolved in hexane and precipitated several times with acetone. Yield 47%. (M_w = 1.26 x10^5 and M_w/M_n = 1.42, measured by GPC).

Materials and Methods.

Melting points of the organic compounds were measured on a Fisher-Johns apparatus and are uncorrected.

Infra red spectra were registered on a Perkin-Elmer 2000 instrument from KBr discs samples or films prepared by casting. NMR spectra were recorded on a Bruker DRX 400 spectrometer at 25 °C from samples dissolved in deuterated chloroform using TMS as internal reference.

Solid-state ^{13}C CP/MAS NMR spectra were recorded at 100.6 MHz in the temperature range 25-55°C. A Bruker DRX 400 instrument equipped with a CP-MAS accessory and variable temperature unit was used. Samples of 200 mg weight were spun at 4 kHz in a cylindrical ceramic rotor. All the spectra were acquired with contact and repetition times of 2 ms and 5 s, respectively and 256 to 1024 transients were accumulated. The spectral width was 31,2 kHz, and the number of data points was 4K. Chemical shifts were externally calibrated against the higher field peak of adamantane appearing at 29.5 ppm relative to TMS.

Calorimetric measurements were performed with a Perkin-Elmer DSC-7 calibrated with indium. Samples of about 5 mg were heated or cooled at rates of 10°C min^{-1} under a nitrogen atmosphere in a range of –40 to 120°C. TGA were achieved on a Perkin-Elmer TGA-7 thermobalance at similar conditions used in DSC from 25 to 500°C.

Gel permeation chromatography (GPC) was performed with a Waters-150C chromatograph operated at 40°C and equipped with four columns connected in series and packed with μstyragel 10^3, 10^4,10^5 and 10^6 Å. THF was used as solvent and the instrument was calibrated with polystyrene standards of known molecular weights.

Results and discussion

The IR and ^{13}C NMR spectra of monomer and its polymer are given in Figures 1 and 2. The IR spectrum of the monomer shows medium and weak alkene peaks at 1635 and 820 cm^{-1} respectively that are not present in the polymer. In addition, as it can be seen in the ^{13}C-NMR spectra (Figure 2) the disappearance of vinyl carbons (134,2 and 128,73 ppm) of the monomer and the appearance of new signals between 43-47 ppm due to methylene and quaternary backbone carbons is consistent with a vinyl polymerization process.

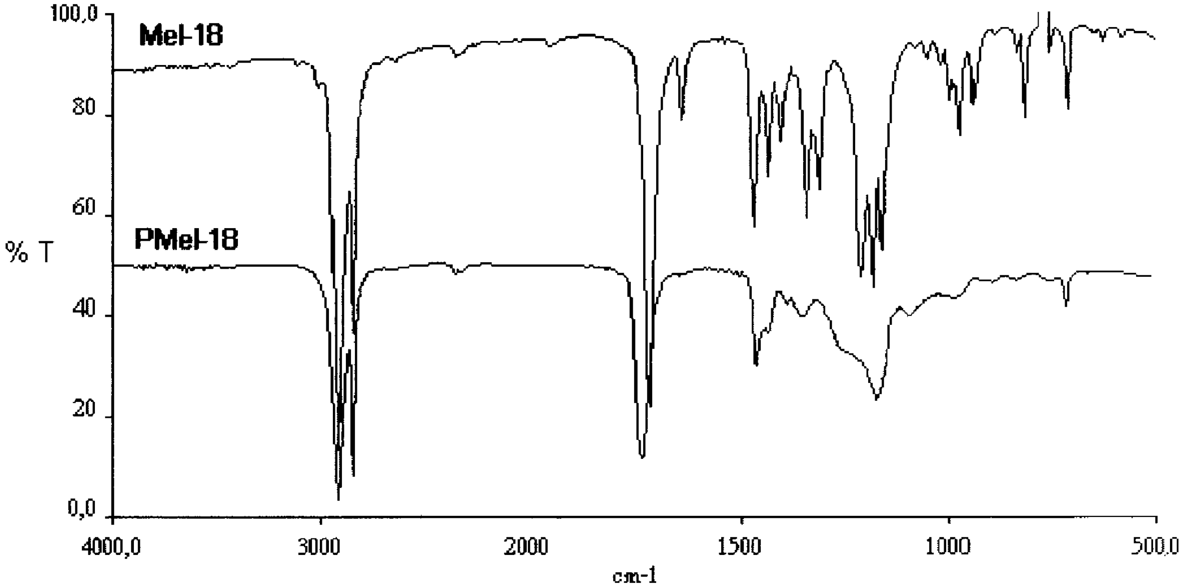

Figure 1. FTIR spectra of MeI-18 monomer (upper trace) and PMeI-18 polymer (lower trace)

Assignment of the ^{13}C NMR peaks for the polymer was made by comparison of this spectrum and those reported in the literature for poly(di-itaconate)s [10,11]. Additionally this figure shows an expanded region of the spectrum corresponding to the two carbonyl carbons (-C-**CO**-OR and -CH_2-**CO**-OR). Each one is split into three peaks due to stereosequences effect at the level of triads (rr, mr and mm). By Lorentzian deconvolution of the signals the molar fraction of the corresponding triads could be calculated (Table 1) and the tacticity of the polymer evaluated.

These results show a predominance of sindiotactic sequences (rr) for PMeI-18 as it would be expected, from a free radical polymerization for a monomer with structure close to the methacrylate monomers. Ours results for PMeI-18 are quite similar to found for poly(dibenzyl itaconate) [10] and poly(di-n-butyl itaconate) [11] although the number average sequence length of sindiotactic sequences found for PMeI-18 is smaller (between 2.21 to 2.54) than the value calculated for poly(dibenzyl itaconate) (4.2) with data from reference [10].

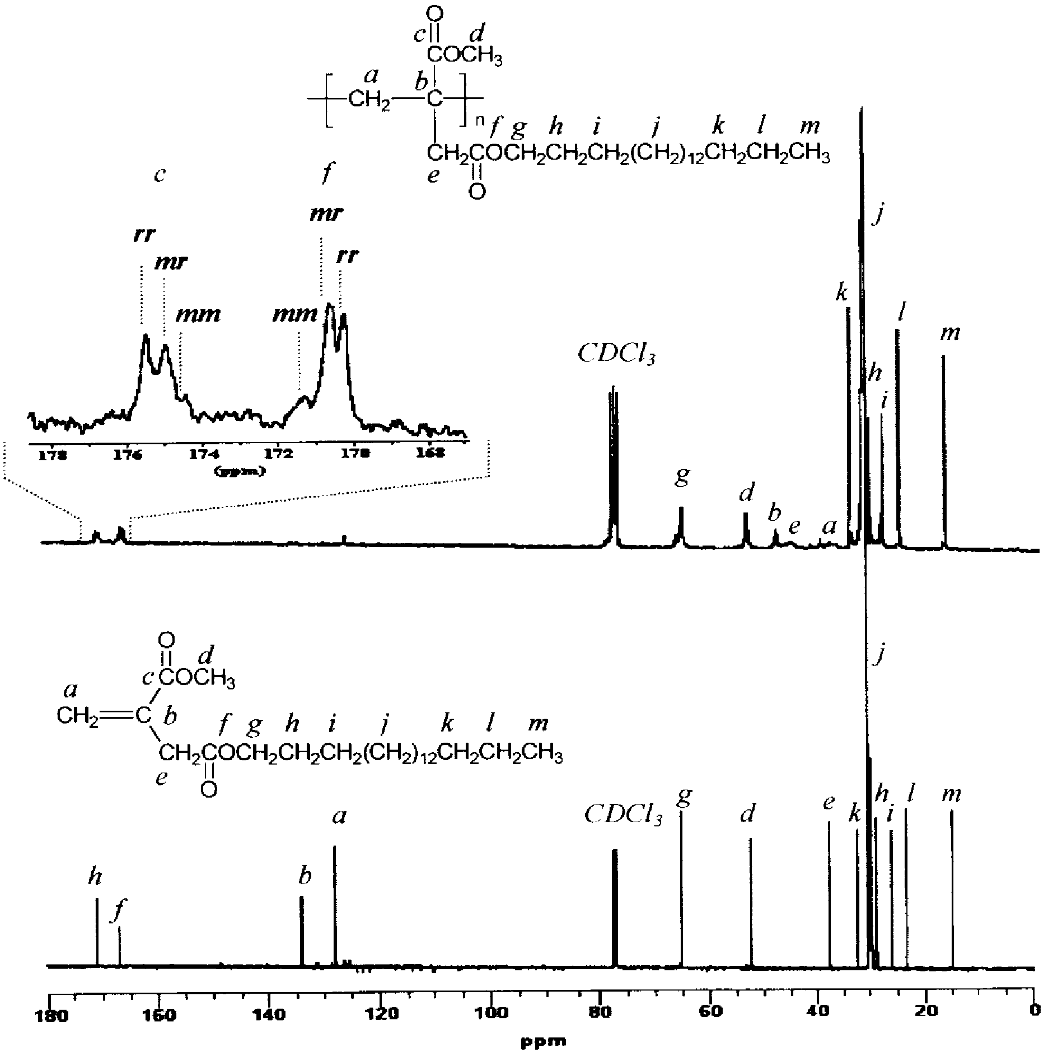

Figure 2. ${}^{13}C$ NMR spectra of MeI-18 (down) and PMeI-18 (top) with peak assignments.

Table 1. Triad and diad tacticity distribution determined from carbonyl carbons in PMeI-18.

-C-CO-OCH$_3$					-CH$_2$-CO-O-C$_{18}$H$_{37}$				
Triad	δ(ppm)	Mole fraction	Diad	Mole fraction	Triad	δ(ppm)	Mole fraction	Diad	Mole fraction
mm	174.5	0.07			mm	171.4	0.15		
mr	175.0	0.58	m	0.36	mr	170.7	0.48	m	0.39
rr	175.5	0.35	r	0.64	rr	170.3	0.37	r	0.61

From results of data shown in Table 1, it is noticeable the difference in triads content obtained for both carbonyl carbons. It may be due to a low resolution of the peaks attained in the spectra that makes difficult to obtain the integral values with accuracy.

On the other hand, TGA experiments proved that this polymer begins a decomposition process with weight-loss above 230°C (Fig. 3 A). Nevertheless before getting this temperature, a reversible endothermic transition with a temperature maximum of 44°C and a ΔH = 4.8Kcal/mol due to the melting of the side chains is observed in DSC traces (Fig. 3 B). It is well known that the *n*-alkyl side chain in polymers are able to crystallize when get a minimum length [16].

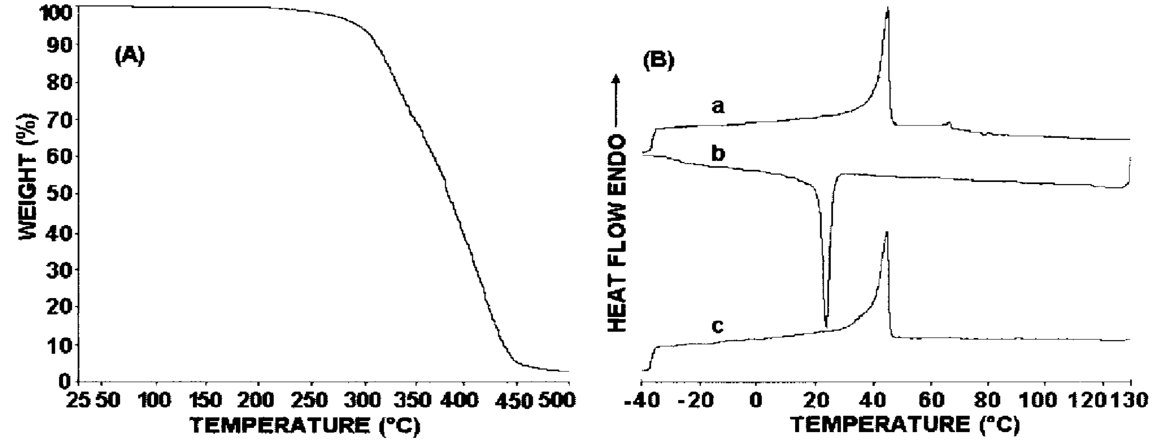

Figure 3. (A) TGA Trace of PMeI-18. (B) DSC traces of PMeI-18 (a) first heating, (b) cooling and (c) second heating .

In order to corroborate this fact, a ^{13}C NMR study in solid state at different temperatures was carried out. It is well established that chemical shift of methylenes in polymethylene chains are highly sensitive to conformation and crystal packing [17].

The spectra were performed at three different temperatures, before, during and after, the transition. Figure 4 shows the ^{13}C CP/MAS NMR expanded spectra of the region where most of the side chain signal appears. The main changes, which can be observed, are the followings:

At 45°C the peak around 33ppm, assigned to the methylenes crystallized in all-trans conformation (c) in Figure 4, vanished and a new peak near 30 ppm, attributable to the methylenes in fast equilibrium between gauche and trans conformations characteristic of molten state emerged. At 55°C the replacement of the peaks is complete. This fact corroborates that the melting of the side chain take place in the transition.

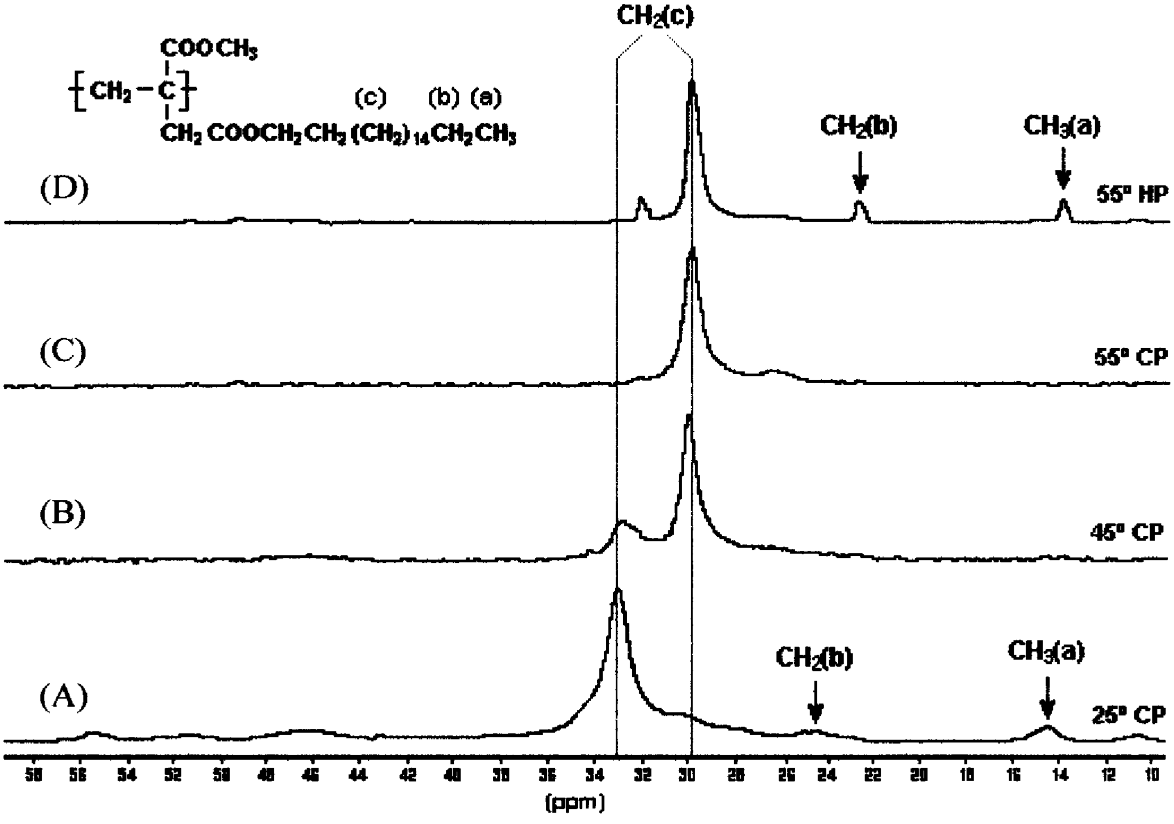

Figure 4. Solid state ^{13}C CP/MAS (A, B, C) and HPDEC/MAS (D) NMR spectra of PMeI-18 at the indicated temperatures.

On the other hand, the chemical shift at 25°C of the methyl and terminal methylene appears at near 14.5 and 24.8 ppm respectively, (a) and (b) in Figure 4 (A). These chemical shifts are near enough to the reported for *n*-alkanes crystallized in hexagonal form and at 55°C are in good agreement with the chemical shift reported for molten state [17].

The DSC and ^{13}C CP/MAS NMR studies confirm that the side chains are able to crystallize and melt near 45°C. It also strongly suggest that those side chains are crystallized in a hexagonal lattice. This type of crystallization was also observed for poly(diitaconate) derivatives [13]. The ΔH value found for PMeI-18 is almost the half of the reported for poly(dioctadecyl itaconate) (9.8 Kcal/mol), which seems reasonable if we considerate that the last has two side chains [13]. Taking into account that an enthalpy average value near 750 cal/mol·CH_2 was found for the hexagonal-to-liquid transition [16], we can conclude that approximately 6 methylenes are able to crystallize in the side chain.

At the moment, further work is developing in ours laboratories with this and others polyitaconates with different side chain lengths in order to obtain more conclusive results.

Acknowledgments

This work has been supported by CONICIT (Grant G-97000594) and CDCHT-ULA (grant C–1030-00-08A). IR and DSC instruments were acquired through the grant NM-08 (CONICIT-BID). We also thanks to Laboratorio Nacional de RMN Nodo ULA, Facultad de Ciencias (Venezuela) for NMR facilities.

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