

# Structural Characterization of Oligomers from the Polycondensation of Citric Acid with Ethylene Glycol and Long-Chain Aliphatic Alcohols

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**ABSTRACT:** The structural characterization of polyesters of citric acid (CA) with ethylene glycol and long-chain aliphatic alcohols (ROH), prepared by the composition of the reaction mixture being adjusted slightly away from stoichiometric equivalence, was performed with <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy. The aliphatic alcohols employed were 1-decanol, 1-dodecanol, and 1-octadecanol. The <sup>13</sup>C-NMR carbonyl region presented four groups of signals, two corresponding to the ester groups and two corresponding to the acid

groups. However, symmetric and asymmetric groups of CA moieties were identified in the <sup>13</sup>C-NMR spectra. The ester yield from ROH decreased as the number of carbon atoms in the alcohols increased. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 302–306, 2003

**Key words:** polyesters; NMR; colloids; step-growth polymerization

## INTRODUCTION

Polyesters of citric acid (CA), which form insoluble crosslinked networks, have been used as polymeric matrices for controlled and sustained drug release<sup>1,2</sup> and as synthetic resins.<sup>3</sup> As far as we know, NMR spectroscopy has not been used to characterize their structure because of their limited solubility in different solvents.

In previous work,<sup>4,5</sup> the polycondensation of CA with ethylene glycol (EG) was performed in the presence of a long-chain aliphatic alcohol (ROH; 1-decyl, 1-dodecyl, or 1-octadecyl alcohol). The proportions of the reagents were chosen under the consideration that the system should not reach the gel point. Under those experimental conditions for the synthesis, oligomers, not polymers, were obtained. These products were soluble in organic solvents and consisted of a mixture of oligomers in which not all the molecules had an aliphatic alcohol moiety; therefore, low proportions of the products were soluble in water, and the rest formed stable colloidal dispersions. The proportion of soluble components decreased as the chain of the aliphatic alcohol increased in size.

The aim of this work was to provide a spectroscopic characterization (<sup>13</sup>C- and <sup>1</sup>H-NMR) of the soluble fractions of polyesters from CA, EG, and aliphatic alcohols [1-decanol (C10), 1-dodecanol (C12), and

1-octadecanol (C18)]. These polyesters were prepared by the composition of the reaction mixture being adjusted slightly away from stoichiometric equivalence.

## EXPERIMENTAL

### Materials

CA was recrystallized from water and dried. EG (BDH, England), C10 (BDH), C12 (Fluka, Switzerland), C18 (BDH), and *p*-toluene sulfonic acid (BDH) were used without further purification.

### Polycondensation

The oligomers were prepared by the heating (at 135°C) of a mixture of CA, EG, ROH, and *p*-toluene sulfonic acid for 8 h under reduced pressure. All the CA–EG–ROH oligomers were synthesized with the same initial molar ratio of functional groups: CA/EG/ROH = 1:0.4:0.02. Two reference products from AC and EG were prepared: CA–EG I (CA/EG = 1:0.4) and CA–EG II (CA/EG = 1:2.25). The concentration of *p*-toluene sulfonic acid was, in every case, 1.25% of all the acid groups.

### Carboxyl end-group analysis

The carboxylic acid concentration in the oligomers was determined by the titration of aqueous colloidal solutions of the products with 0.25N NaOH, with phenolphthalein used as an indicator.

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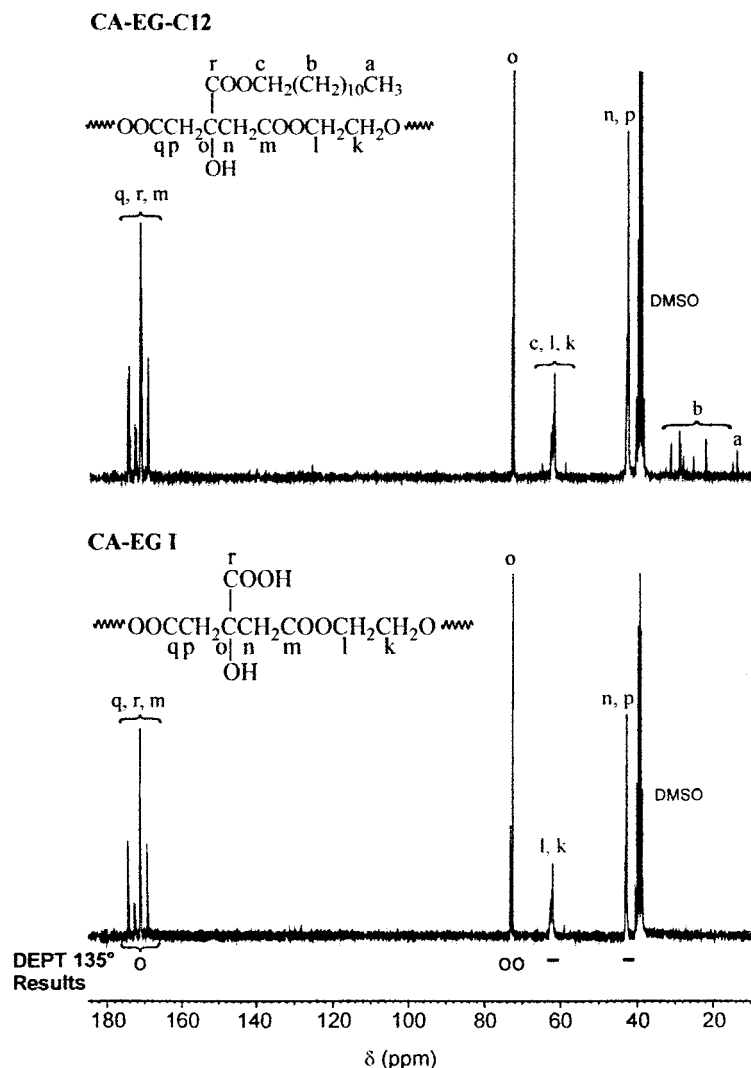


Figure 1  $^{13}\text{C}$ -NMR spectra of CA-EG I (DEPT  $135^\circ$ ) and CA-EG-C12 in  $\text{DMSO}-d_6$ : (O) no signal and (-) negative signal.

### NMR spectroscopy

NMR spectra were recorded with a Bruker AC 250F FT NMR spectrometer (Germany) at the frequencies of 250 ( $^1\text{H}$ ) and 62.5 MHz ( $^{13}\text{C}$ ). The polymers were dissolved in dimethyl sulfoxide- $d_6$  ( $\text{DMSO}-d_6$ ) in 5-mm-outside-diameter tubes. The nature of each atom was determined with the distortionless enhancement by polarization transfer (DEPT) technique with proton pulses at  $135^\circ$ .

## RESULTS AND DISCUSSION

### Polycondensation

Because of the stoichiometric imbalance of the  $-\text{COOH}/-\text{OH}$  molar ratio used in the reactions, the formation of long-chain polymers was avoided, and only oligomers were produced. Moreover, an excess of acid groups was used in the polycondensation with the aim of facilitating the incorporation

of the aliphatic long-chain (R) alcohols in the polymer. The obtained oligomers formed colloidal dispersions in water.<sup>4</sup>

### Structural characterization

The structural characterization of the products was accomplished by  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR spectroscopy. All signals in the spectra appear as groups of signals because of the existence of oligomers with different chain lengths. This originated from differences in the environment of the carbon atoms and, consequently, changes in the chemical shifts. The  $^{13}\text{C}$ -NMR signal assignments of CA-EG I were supported with the DEPT  $135^\circ$  technique. The  $^{13}\text{C}$ -NMR spectra of CA-EG I and CA-EG-C12, along with their signal assignments, are shown in Figure 1.

The spectrum of CA-EG I shows four groups of signals. The first one consists of three signals at 42.5, 42.6, and 42.8 ppm that arise from the carbon atoms p

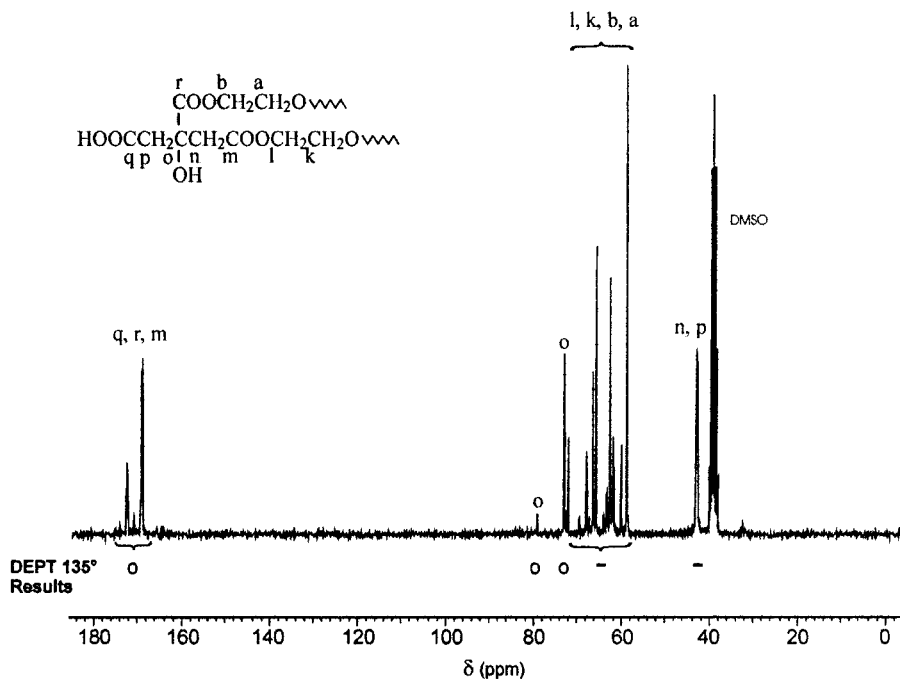


Figure 2  $^{13}\text{C}$ -NMR spectrum of CA-EG II in  $\text{DMSO-}d_6$  (DEPT 135°): (○) no signal and (−) negative signal.

and n of the oligomer sequence displayed in Figure 1. The second group has two signals at 61.7 and 62.2 ppm, which correspond to carbon atoms k and l. The third group consists of two signals at 72.3 and 72.8

ppm that are attributed to the quaternary carbon o. The lowest field signals correspond to carbonyl carbon atoms. These latter assignments are discussed in more detail later.

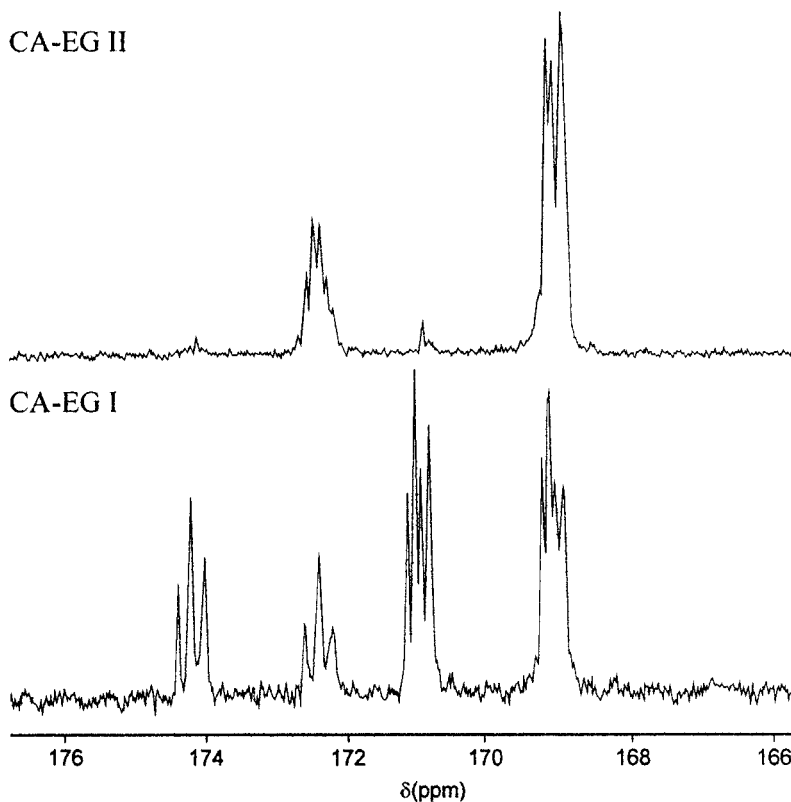


Figure 3  $^{13}\text{C}$ -NMR spectra of CA-EG I and CA-EG II in  $\text{DMSO-}d_6$ : carbonyl region.

TABLE I  
Percentage of Acid and Ester Carbonyl Groups in Oligomers

Products	$A_{174.5}$	$E_{172.5}$	$A_{171.0}$	$E_{169.0}$	Acid groups	
					From titration	From $^{13}\text{C-NMR}$
CA-EG I	19.6	9.8	43.1	27.5	61.1	62.7
CA-EG-C10	18.3	12.0	37.0	32.0	56.1	55.3
CA-EG-C12	18.8	10.6	41.0	29.6	62.4	59.8
CA-EG-C18	20.0	10.0	43.3	26.7	62.4	63.3
CA-EG II	0	28.5	2.5	69.0	4.1	2.5

The  $^{13}\text{C-NMR}$  spectrum of CA-EG-C12 (Fig. 1) presents the same signal pattern observed in the spectrum of CA-EG I, but it shows some additional signals between 13 and 31 ppm due to carbon atoms of the R moiety incorporated into the polyester. The signal at 13 ppm is assigned to the carbon atom of  $\text{CH}_3$ . The group of signals labeled b in Figure 1 corresponds to the  $n\text{-CH}_2\text{—}$  sequence, except for those next to the  $\text{—CO}_2\text{—}$  group, which appear in the group of signals at 62 ppm.

The  $^{13}\text{C-NMR}$  spectra of CA-EG-C10, CA-EG-C12, and CA-EG-C18 differ only in the regional characteristic of the aliphatic signals of R, between 13 and 31 ppm. These signals become weaker as the number of carbon atoms in R increases, suggesting that the yield of ester resulting from the reaction of ROH with  $\text{—COOH}$  groups decreases as the length of R increases. Therefore, it was necessary to accumulate 27,000 pulses to register the spectrum of CA-EG-C18.

The  $^{13}\text{C-NMR}$  spectrum of CA-EG II presents all the signals displayed in the CA-EG I spectrum and some additional signals in the region of 60–80 ppm (Fig. 2). It was possible to assign these signals to the carbon atoms of glycol fragments with the DEPT  $135^\circ$  technique.

### Carbonyl region

$^{13}\text{C-NMR}$  spectra of all the aforementioned oligomers exhibit four groups of signals in the carbonyl region at 169.0, 171.0, 172.5, and 174.5 ppm. The relative intensities of the signals depend on the  $\text{—COOH/—OH}$  molar ratio used in the polycondensation. The spectra of the reference oligomers CA-EG I (prepared with an excess of  $\text{—COOH}$ ) and CA-EG II (prepared with an excess of  $\text{—OH}$ ; Fig. 3) were analyzed for the assignment of the carbonyl signals.

The oligomer CA-EG II possesses the higher ester/acid group ratio because of the excess of EG used in its preparation, and its spectrum shows a lower intensity of the signals at 171.0 and 174.5 ppm in comparison with the spectrum of CA-EG I. This result points out that the groups of signals at 171.0 and 174.5 ppm correspond to the carbonyl carbons of the acid groups and that the other two signals at 169.0 and 172.5 ppm

are due to the carbonyl carbons of the ester groups. All these carbon atoms have similar nuclear Overhauser effects and spin-lattice relaxation times.<sup>6</sup> Therefore, the percentages of acid carbonyl groups ( $A_{171}$  and  $A_{174.5}$ ) and the percentages of ester carbonyl groups ( $E_{169}$  and  $E_{172.5}$ ) can be calculated from the intensities of the signals of the carbonyl groups. The sum of  $A_{171}$  and  $A_{174.5}$  is likely to be equal to the percentage of acid groups in the oligomers. These values and the percentages of acid groups determined by titration are compared in Table I. The coincidence of both values confirms the proposed signal assignment.

The small values encountered for acid groups in CA-EG II indicate that the conversion of these carboxylic acid groups into ester groups was almost complete. The determination of acid groups for CA-EG II, with both titration and  $^{13}\text{C-NMR}$  methods, was ac-

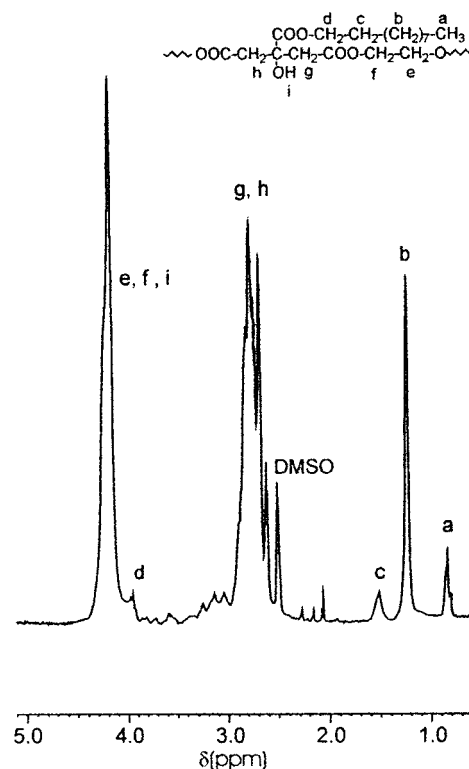


Figure 4  $^1\text{H-NMR}$  spectrum of CA-EG-C12 in  $\text{DMSO-}d_6$ .

TABLE II  
Yield of Ester from ROH Determined  
by  $^1\text{H-NMR}$  Spectroscopy

Product	R/CA theoretical	R/CA experimental	Yield (%)
CA-EG-C10	0.21	0.18	85
CA-EG-C12 <sup>4</sup>	0.27	0.16	63
CA-EG-C18	0.45	0.02	4

accompanied by larger errors because of the difficulties in obtaining the integration values from very weak signals in the  $^{13}\text{C-NMR}$  spectrum and the difficulties met in the titration of a product with low contents of acid groups.

It is possible to distinguish between symmetrical and asymmetrical carbonyl groups by a comparison of the intensities of the signals due to acid and ester groups. Indeed, the  $A_{171.0}$  values shown in Table I are approximately twice as large as the  $A_{174.5}$  values. A similar trend can be observed for the  $E_{169.0}$  and  $E_{172.5}$  values. These results suggest that the signals at 171 and 169 ppm correspond to carbonyl carbon atoms of symmetrical groups of CA moieties, whereas the acid and ester asymmetrical groups resonate at 174.5 and 172.5, respectively.

### Long-chain aliphatic moiety

The incorporation of the R moiety into the oligomers by ester linkages depends on the length of R. Therefore, the yield of  $-\text{CO}_2\text{R}$  could be estimated from  $^1\text{H-NMR}$  (Fig. 4) with the ratio of the signal intensities of  $-\text{CH}_2-$  groups from R at 1.2 ppm and those of CA at 2.8 ppm, as previously reported.<sup>4</sup> The results are shown in Table II.

It can be observed in Table II that the yield of the  $-\text{CO}_2\text{R}$  groups decreases as the number of C atoms in R increases. This behavior is rather unexpected if we consider that the reactivity of  $-\text{CO}_2\text{H}$  and  $-\text{OH}$

groups is likely to be independent of the substituting group.<sup>7</sup> A possible explanation could be ascribed to the increasing lack of homogeneity in the reaction mixture as ROH becomes more insoluble as the length of R increases. Therefore, the approach of ROH to  $-\text{CO}_2\text{H}$  groups is hindered; consequently, the yield of ester bonds diminishes.

### CONCLUSIONS

The polyesterification of CA, EG, and ROH, with the composition of the reaction mixture slightly away from stoichiometric equivalence, yielded oligomers that could be characterized in solution by  $^1\text{H-}$  and  $^{13}\text{C-NMR}$  techniques. The signals of the carboxylic region of the spectra were assigned to the acid groups at  $\delta = 171.0$  and  $\delta = 174.5$  ppm and to the ester groups at  $\delta = 169.0$  and  $\delta = 172.5$  ppm. The signals at 171 and 169 ppm correspond to the carbonyl carbon atoms of symmetrical groups of CA moieties, whereas the acid and ester asymmetrical groups resonate at 174.5 and 172.5.

The proportion of  $-\text{CO}_2\text{R}$  in the polyester decreases as the number of C atoms in R increases.

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