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STUDY OF DIOXOLANE-DIOXEPANE COPOLYMERS THROUGH IR AND DSC

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Summary

The composition of the copolymers of 1,3-dioxolane with 1,3-dioxepane was investigated using FT-IR and DSC. The first method produce accurate values for the overall composition, the later allows discriminating between the copolymer and the mixture of homopolymers.

INTRODUCTION

Investigating the microstructure of co-poly-acetals is a rather subtle problem as the products obtained through cationic copolymerization of cyclic acetals may be suspected of being blends of homopolymers. Moreover, a mixture of homopolymers may produce (through transfer reactions to polymer - transacetalisations) macromolecular chains characterized by a symmetrical distribution of molecular weight similar to a random copolymerization [1], or block-copolymers [2] as a function of the basicity of the polymer chains involved.
As a result of copolymerization of 1,3-dioxolane (DXL) with 1,3-dioxepane (DH), the following sequences may be formed:

- *ethylene-acetal-ethylene, in the case of poly-dioxolane (PDX)*

$$\sim O-(CH_2)_2-O-CH_2-O-(CH_2)_2-O-CH_2\sim$$

- *butylene-acetal-butylene, in the case of poly-dioxepane (PDH)*

$$\sim O-(CH_2)_4-O-CH_2-O-(CH_2)_4-O-CH_2\sim$$

- *ethylene-acetal-butylene, in the case of the copolymer DXL-DH*

$$\sim O-(CH_2)_2-O-CH_2-O-(CH_2)_4-O-CH_2\sim$$

Such reduced structural differences lead to difficulties in finding the microstructure for the copolymers DXL-DH. Their composition and microstructure is usually determined by the ^{1}H and ^{13}C NMR spectra, method expensive and not always available.

The present work investigates the use and limits of two widely accessible methods, the Fourier Transform Infrared Spectroscopy (FT-IR) and the Differential Scanning Calorimetry (DSC) to characterize the microstructure and composition of DXL-DH copolymers.

EXPERIMENTAL PROCEDURES

The homopolymers of DXL and DH have been obtained by a previously described method [3-5]. Homopolymer mixtures with pre-established compositions (expressed by the molar fraction of DH repeat units, f_{DH}) have been obtained by dissolving the corresponding amounts from each homopolymer in acetone, at a total concentration of 5% by weight. Subsequently, the samples have been evaporated and dried at 0.1 torr and 35°C during 24 hr.

The copolymers used have been synthesized using the same technique as for homopolymers; their final composition has been appreciated according to a mass balance, knowing the concentrations of unreacted monomers (measured through gas chromatography [3-5]) as well as the initial monomer concentrations.

To assure the uniformity of all samples, copolymers have also been dissolved in acetone at a concentration of 5% by weight and then submitted to the same treatment as the homopolymers.

FTIR spectra have been recorded with a spectrophotometer ATI-Mattson Genesis Series Model 9423, at 25°C, using an ATR (attenuated total reflection) device with a window of zinc selenide and making 200 scans/spectrum. Since the polymers are waxy, they have been placed directly on to the ATR device.

DSC thermograms have been recorded with a Setaram DSC 131 apparatus in air. The samples have been put into the DSC crucibles and then maintained at 40°C and 0.1 torr for 24 hours, prior of DSC measurements. The thermograms were recorded at 5°C/min in N_2 and the glass transition was determined at the inflexion point.

RESULTS

Comparing the IR spectra of the homopolymers obtained by us with literature data [6] we did not notice any differences. Likewise, comparing the spectrum of a polymer mixture with that of a copolymer (Fig. 1) having the same total composition (f_{DH} = 0.19) we did not record any difference regarding the positions and intensities of peaks in the two corresponding spectra. This fact let us to use polymer mixtures for building a calibration curve subsequently used to evaluate copolymer compositions.

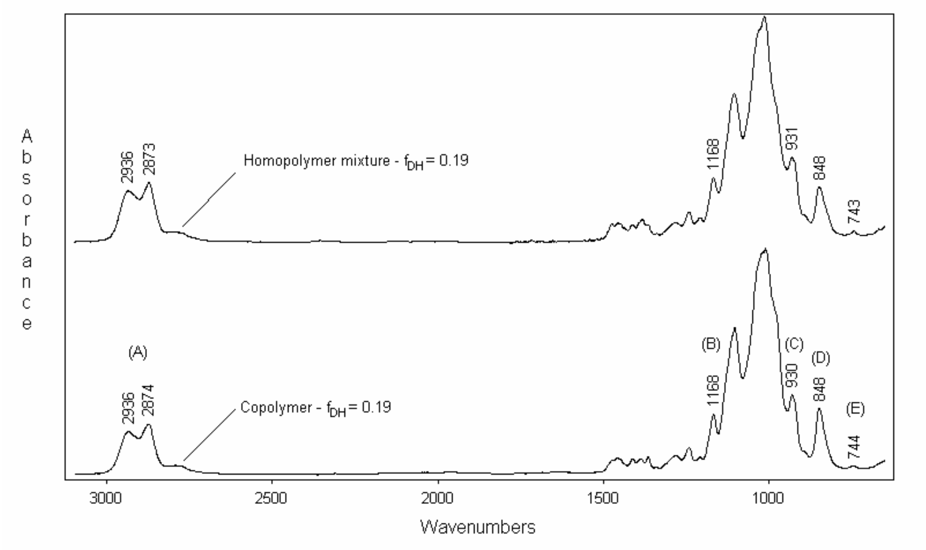

Fig. 1. FTIR spectra for a mixture of polydioxolane-polydioxepane and for a copolymer, respectively

The following peaks have been used for calibration:

(A) a doublet at 2936 - 2872 cm^{-1} (stretching of -CH_2- and -CH_3) [7];

(B) the absorption at approximately 1165 cm^{-1}, very likely a vibration of symmetrical stretching -C-O- in ethers and acetals (takes part in a characteristic triplet or quadruplet at approx. 1200 - 950 cm^{-1}) [8,9];

(C) the vibrations in the zone 950 - 900 cm^{-1} (asymmetric stretching of the group -C-O- from ethers and acetals) [8,9];

(D) the vibrations from approximately. 800 - 790 cm^{-1} (likely characteristic for the group -O-C-O-) [10,11];

(E) the vibration from 743 cm^{-1} (rocking of the sequence-C-C-C-C- (C_4) or for more than four consecutive carbon atoms) [12].

Table 1. Molar fraction of poly-dioxepane for several mixtures of poly-dioxolane and poly-dioxepane used for calibration

Sample	PDX	A1	A2	A3	A4	A5	PDH
f_{PDH}	0	0.125	0.25	0.5	0.75	0.875	1

PDX - poly-dioxolane; PDH - poly-dioxepane; $A_1 \div A_5$ - homopolymer mixtures;
f_{PDH} - molar fraction of poly-dioxepane in mixture.

The ratios of the absorption peak surfaces, measured for the mixtures having the composition given in table 1 have led to the calibration curves (Fig. 2).

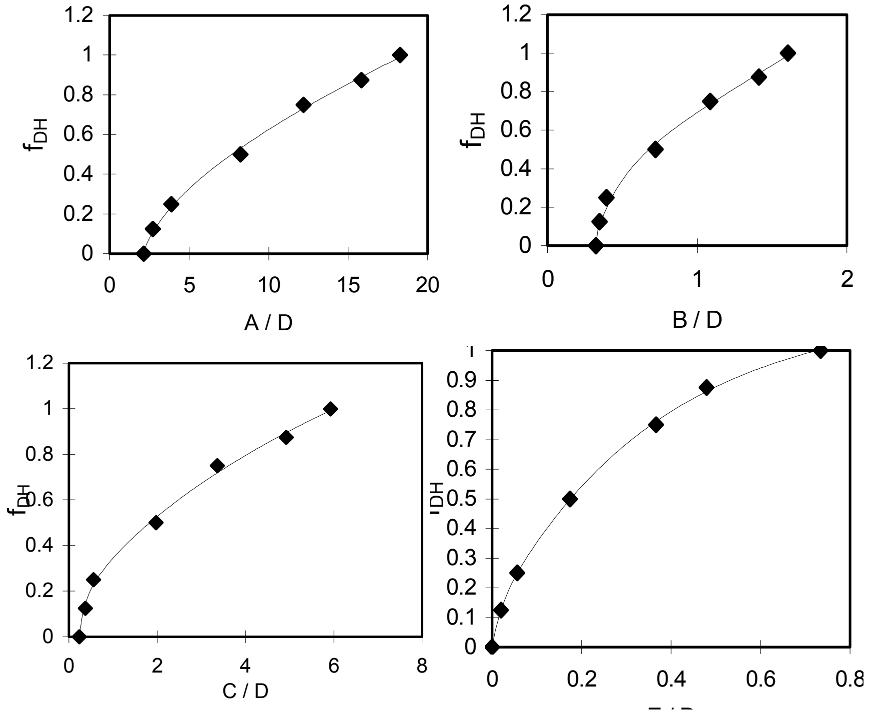

Fig. 2. Calibration curves - correlation between the molar fraction of DH units (f_{DH}) and the surface ratio for some characteristic IR absorption peaks.

Copolymer compositions have been calculated as an average of the measured compositions resulting from the four calibration curves; the resulted averages for the polymers investigated are given in table 2.

Table 2. Results of FT-IR and DSC analyses for homopolymers and copolymers

Sample	Tg (°C)	f_{DHsp}	Sample	T_g (°C)	f_{DHsp}
PDH	-78.1	1	P_6	-71.6	0.27
P_1	-79.9	0.72	P_7	-69.3	0.26
P_2	-72.3	0.50	P_8	-74.2	0.19
P_3	-75.5	0.41	P_9	-69.1	0.14
P_4	-69.9	0.34	P_{10}	-68.2	0.10
P_5	-72.6	0.30	PDX	-67.5	0

$P_1 \div P_{10}$ - copolymer samples with several compositions;
PDH - poly-dioxepane; PDX - poly-dioxolane;
Tg - glass transition temperature (°C);
f_{DHsp} - molar fraction of dioxepane units, measured from IR spectra.

DSC measurements have shown that for homopolymer mixtures, both, glass transition temperature (Tg) and melting temperature are present in the thermograms. Temperature corresponding to melting-crystallization transitions depends upon composition. The copolymers with a molar fraction of the comonomer higher than 0.1 exhibit no melting-crystallization transition.

However, glass transition temperatures (Tg) depend in a linear manner upon copolymer composition, between the values Tg corresponding to homopolymers (see table 2 and figure 3). Considering the scattering of the experimental points, the unknown copolymer composition can be roughly evaluated from the equation:

$$T_g = - 12{,}712 \cdot f_{DH} - 66{,}09 \qquad (1)$$

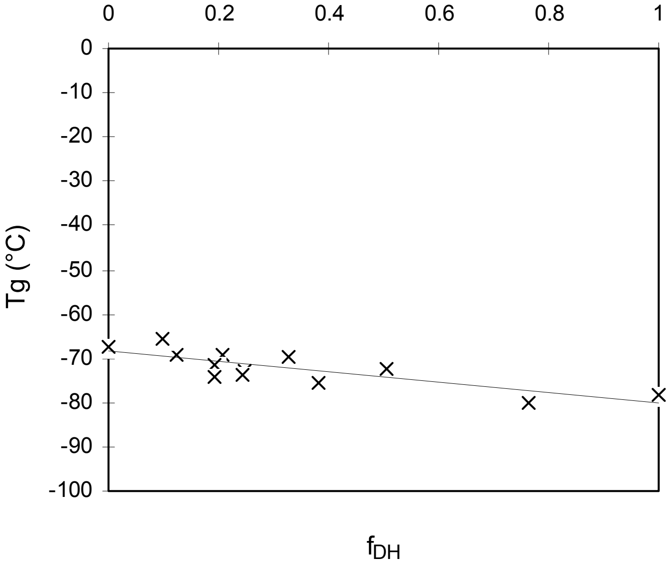

Fig. 3. Variation of Tg with molar fraction of DH, estimated from IR spectra (f_{DH})

CONCLUSIONS

FT-IR Spectroscopy allows the non-destructive measurement of the composition of DX-DH copolymers or of the corresponding homopolymer mixtures PDX and PDH respectively, without being able to distinguish between a copolymer and a homopolymer mixture. A calibration is necessary, prior to measurements

From the DSC thermograms it becomes possible to discern between a copolymer and a homopolymer mixture, through the absence or presence of melting transitions. Considering the equation of the straight line corresponding to the variation of Tg with the molar fraction of DH repeat units in copolymer, it is possible to estimate the composition of an unknown sample without a calibration.

The methods can be used in conjunction, to validate the obtained value by checking it against that already obtained through the other method.

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