



SYNTHESIS AND MOLECULAR MECHANICS CALCULATION OF COPOLYESTERS

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ABSTRACT

Copolyesters and polyesters are similar as both have carboxylate ester in the repeating copolymers of a diol and diacid. In the present work, copolyesters based on adipoyl chloride with aromatic and aliphatic diols were synthesized by solution polycondensation method. To ascertain the quality of the synthesized copolyester materials, a satisfactory vibrational band assignments has been made for some of the specific modes of vibration observed from FTIR spectra. The assignments are very well supported by Laser Raman spectral studies and molecular mechanics calculations.

Key words : Copolyesters, FT-IR spectra, Molecular mechanics

INTRODUCION

Polyesters are one of the most important class of polymers in use today with repeating carboxylate groups in their backbone chain. During nineteen thirties, Carothers and Natt¹ created modern chemistry and technology of polyesters. Polyester is defined as long chain polymers chemically composed of atleast 85% by weight of an ester and a dihydric alcohol. All techniques used in preparing low molecular weight esters have been utilized to prepare polyesters. In addition, many different polycondensation techniques including interfacial, melt, emulsion and solid state polycondensation have been reported²⁻⁸. The techniques used for polymerization depend on the nature of the monomer, the type of polymerization mechanism chosen, the required physical form of the material and the viability of the process for industrial production. The important features of solution polycondensation are high yield, moderate slow reaction, adequate solvent and degree of mixing and stirring, selection and control of temperature and absence of side reactions. Hence, in the present work, solution polycondensation method has been adopted for the synthesis of copolyesters viz., PBRA and PEQA.

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EXPERIMENTAL

Synthesis of copolyesters

A primary requisite of high polymer formation is that the solvent must dissolve or swell the polymer sufficiently to permit completion of the polymerization. The reagents, solvents and carrier gas must be well dried. Traces of moisture hydrolyse the acid chloride and block the reaction⁹.

Synthesis of poly[oxy – (1,4-butylene) –oxy-adipoyl – co-oxy – (1,3- phenylene) – oxyadipoyl] (PBRA)

A 500 mL three necked round bottom flask equipped with a magnetic stirrer, nitrogen inlet, thermometer, reflux condenser with guard tube was charged with 1 mole of resorcinol, 2 moles of 1,4- butane diol, 3 moles of adipoyl chloride and 150 mL of 1,2-dichlorobenzene. The mixture was heated to reflux for 25-30 hrs at 140-160 °C in nitrogen atmosphere with constant stirring and cooled to get pure dry dull brown copolyester. The yield was 60-65%.

Synthesis of poly [oxy– (ethlyene) –oxy-adipoyl – co-oxy –(1,4 -phenylene) – oxy-adipoyl] (PEQA).

In the same experimental set up as above a mixture of 1 mole of resorcinol, 2 moles of 1,4- butanediol, 3 moles of adipoyl chloride and 150 mL of 1,2-dichlorobenzene was heated to reflux for 25-30 hrs at 140-160 °C to get PEQA.

RESULTS AND DISCUSSION

FTIR Spectral analysis

The IR spectra of copolyesters were recorded using Perkin-Elmer spectrophotometer in the frequency region 4000-500 cm^{-1} . KBr pellet technique was employed for recording the IR spectra of copolyesters.

Molecular mechanics calculation

Molecular mechanics calculation is an empirical calculational method intended to give estimates of structures and theoretical frequencies of molecules. In the present work, MM study was carried out for the representative copolyesters PBRA and PEQA to obtain the theoretical frequencies. Some of the specific modes of vibrations observed in the FTIR and Laser Raman spectra of copolyesters PBRA and PEQA are in good agreement with the

theoretical values thereby confirming the correctness of the functional groups and is presented in Tables 1 and 2.

Table 1. A comparative study on theoretical and observed vibrational frequencies of PBRA

Calculated values	Frequency (cm ⁻¹)		Vibrational band assignment
	Observed values		
	FTIR	Laser Raman	
3679 (vw)	3600 (w)		Free -OH group
3052 (m)	3050 (s)		Aromatic C-H asymmetric stretching
3013 (m)	3010 (s)		Aromatic C-H symmetric stretching
2929 (m)	2924 (s)	2923 (m)	Aliphatic C-H asymmetric stretching
2819 (s)	2800 (s)		Aliphatic C-H symmetric stretching
1699 (vs)	1697 (vs)	1630 (vs)	>C=O stretching of ester
1616 (w)	1600 (w)		Aromatic C≡C stretching
1287 (m)	1281 (s)	1312 (s)	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O} \end{array}$ stretching of ester
1187 (w)	1195 (s)		CH ₂ wagging
1165 (w)	1153 (s)		Aromatic C-H in-plane deformation of 1,3-disubstituted benzene
1042 (w)	1040 (m)	1089 (s)	C-O stretching of ester

Table 2. A comparative study on theoretical and observed vibrational frequencies of PEQA

Calculated values	Frequency (cm ⁻¹)		Vibrational band assignment
	Observed values		
	FTIR	Laser Raman	
3682 (vw)	3600 (vw)		Free -OH group
3054 (m)	3049 (s)	3070 (w)	Aromatic C-H asymmetric stretching
3015 (m)	3012 (s)		Aromatic C-H symmetric stretching
2949 (vs)	2959 (s)		Aliphatic C-H asymmetric stretching
2885 (s)	2882 (w)	2550 (m)	Aliphatic C-H symmetric stretching
1709 (vs)	1697 (vs)	1613 (s)	>C=O stretching of ester
1516 (s)	1516 (m)		Aromatic C=C stretching
1448 (w)	1450 (m)		Aromatic C=C stretching
1427 (m)	1427 (s)		α -Methylene C-H scissoring of ester
1289 (vs)	1281 (s)	1312 (s)	$\begin{array}{c} \text{O} \\ \\ \text{---C---O} \end{array}$ stretching of ester

vs- very strong; vw – very weak; s – strong; w – weak; m-medium

In the present investigation, a detailed work is done on the analysis of vibrational bands to confirm the structure of repeating units of the synthesized copolyesters.

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