

Microwave-Assisted Synthesis and Characterization of Random Copolyesters

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Abstract: Synthesis and characterization of polyesters containing chalcone chromosphers were carried out and their properties were studied. Chalcones are 1,3-diphenyl-2-propene-1-one in which two aromatic rings linked by a three carbon α,β - unsaturated carbonyl system. Synthesis has been carried out using microwave. The MW-assisted synthesis of co-polyesters has been effected using from propane1, 3-diol and 1,4-cyclohexane dimethanol with various carboxylic acids in the presence of titanium isopropoxide as the catalyst. Microwave structural analysis and thermal properties of biodegradable diblock copolyesters were also performed. The synthesized polymers were characterized by solubility measurement and intrinsic viscosity methods. Results are presented and discussed.

Keywords: Poly(propane1,3-diol fumaric acid1,4-cyclohexanedicarboxylic acid), Poly(1,4-cyclohexanedimethanol fumaric acid 1,4-cyclohexanedicarboxylic acid), Poly(propane1,3-diol fumaric acid 1,4-cyclohexanedimethanol), Poly condensation

Introduction

The family of polyesters comprises all polymers with ester functional groups in the polymer back bone¹. In principle, the synthesis of polyesters or esters in the presence of large amount of water has only been studied by a few research groups. Saam *et al.*²⁻⁴ studied the poly condensation in suspension of hydrophobic diol and diacid compounds using different sulfonate surfactants. They defined the principles of such polycondensation and showed that polyesters of low molecular weight could be obtained in aqueous media. More recently, Manabe *et al.*⁵⁻⁷ studied the esterification of hydrophobic mono-functional compounds in aqueous suspension. Copolyesters, obtained from a multiplicity of reactions having the component groups linked in a random or statistical order, are termed random co polyesters. They retain their strength, clarity and other mechanical properties, despite being exposed to a variety of chemicals that typically affect other materials, such as polycarbonates.

This includes their versatility and flexibility which enhances their application effectively in the design of high-volume, low cost parts as well as critical, more expensive component parts. Phase transfer catalysis is a synthetic technique which involves transport of an organic or inorganic salt from a solid or aqueous phase into an organic/liquid phase where reaction with an organic soluble substrate takes place. Chalcones are 1, 3-diphenyl-2-propene-1-one, in which two aromatic rings are linked by a three carbon α , β -unsaturated carbonyl system. They possess conjugated double bonds and a completely delocalised π -electron system on both benzene rings⁸. Molecules possessing such system have relatively low redox potentials and have a greater probability of undergoing electron transfer reactions. Most of the research studies involved only the polymers with side chain chalcone units. There are only few reports on soluble polymers with chalcone units in the main chain. Incorporation of flexible aliphatic chain segments into the polymer backbone improves the solubility. The present work deals with the synthesis and characterization of polyesters containing chalcone chromospheres in the main chain and study of their properties.

Experimental

Melting points were determined with open capillary tube on a Gallenkamp (variable heater) melting point apparatus and were uncorrected. Infra red spectra were recorded as KBr pellets on a buck spectrometer. ¹H and ¹³C NMR were run on a Bruker-AC-250 and JEOL-JNM-GX 300-MHz spectrometer (in ppm relative to Me₄Si and H₃PO₄). The elemental analysis (C, H, N) of compounds were performed using a carbon-hydrogen elemental analyzer. The microwave-assisted syntheses were carried out in domestic oven, Panasonic 400 W. Solvents used were of reagent grade and when necessary, were purified and dried by standard methods.

Microwave method

The reaction mixture was taken in round-bottom flask placed in a microwave oven and irradiated at 400 W for 20 min with addition of catalyst TTiPO. The solid product was dried and dissolved in chloroform then filtered and re-precipitate from methanol.

Synthesis of polyesters

The MW-assisted synthesis of co-polyesters from propane 1, 3-diol and 1, 4-cyclohexane dimethanol with various carboxylic acids in the presence of titanium isopropoxide as the catalyst. The influence of reaction time, reaction temperature, catalyst concentration and monomer ratio on the polymer yield and the molecular weight studied for bulk and solution poly condensation. A reaction temperature of 29 °C two dicarboxylic acid/diol ratio of 1:1:2 and a MW irradiation time of 20 min on 300-500 W. A comparison with conventional heating under these conditions. Showed 10 fold increases of reaction rate under MW conditions.

Results and Discussion

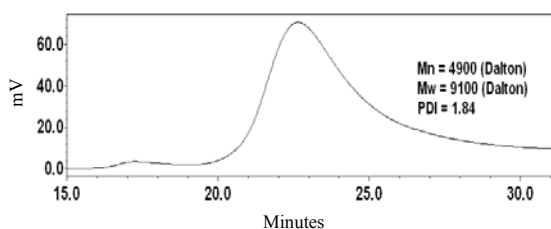
Molecular weight

In order to improve the thermal and mechanical properties of the poly (estercarbonate)s, chain-extension products (PCDMFCDC, PPFCDCM and PPFCDC) were also synthesized starting from dihydroxy-terminated oligomers obtained by the etherification of succinic acid in the presence of 1,3-propanediol and 1,4-cyclohexanedimethanol (PCDMFCDC, PPFCDCM and PPFCDC)⁹. Molecular weights and molecular weight distributions of the polymers obtained, as well as the transition temperatures are reported in Table 1.

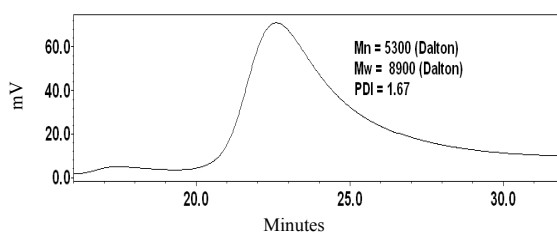
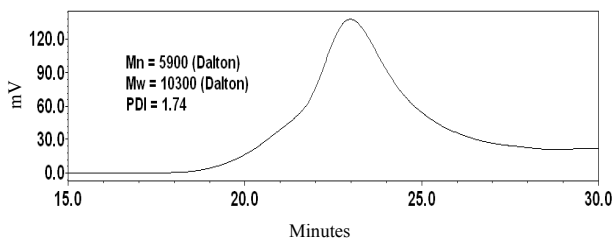
Table 1. Molecular and thermal characterization of poly (ester-carbonates)

S. No	Sample	\overline{M}_n	\overline{M}_w	PD	T_g °C	T_m °C	DH J/g
1.	PCDMFCDC	5900	10300	1.74	67.47	95.27	27.81
2.	PPFCDM	4900	9100	1.84	62.30	96.67	14.46
3.	PPFCDC	5300	8900	1.67	61.77	97.29	13.55

Molecular weights of the long chain branched low T_g polyesters were characterized using Size Exclusion Chromatography (Table 1). Characterization of the molecular weight and branching index indicated that synthesis of long chain branched low T_g polyesters in the presence of mono functional reagents retarded gel formation and permitted synthesis of gel free polymers having higher degrees of branching. Moreover, the presence of end cappers allowed incorporation of TMT up to 3.2 mol %. As shown in Table 1, reaction of higher levels of tri functional reagent resulted in synthesis of polymers with higher degrees of branching as depicted from the lower branching index values. Moreover, incorporation of poly (propylene glycol) mono butyl ether as the mono functional long chain end capper resulted in lowering the glass transition temperature of the low T_g polyesters. Adhesive testing of the samples using peel testing. Size exclusion chromatogram of three different polymers is shown in Figure 1-3 with polydispersity index.

**Figure 1.** Poly(propane1,3-diol fumaric acid 1,4-cyclohexanedimethanol) (PPFCDM)

As the molecular weight increases mechanical strength increases. At low temperatures the polymer behaves like a glass. Molecular weights of these polymers are low and hence these cannot find applications as acrylic polymers where they are used as adhesives.

**Figure 2.** Poly(propane1,3-diol fumaric acid 1,4-cyclohexanedicarboxylic acid) (PPFCDC)**Figure 3.** Poly(1,4-cyclohexanedimethanol fumaric acid 1,4-cyclohexanedicarboxylic acid) (PCDMFCDC)

Viscosity measurement

The inherent viscosity of the resulting polymers was determined in dimethyl sulphoxide solution at 30 °C using Ubbelohde viscometer. In each case, 25 mg of dry pure copolyester sample was dissolved in 25 mL of DMSO, kept aside for some time with occasional shaking. The η_{inh} was calculated from the flow time measurement. The inherent viscosity values of all the copolyesters are listed in Table 2. The data reveals that these polymers are of reasonably high molecular weight. The viscosities of solutions of the polymers in chloroform were measured at 25 °C using an Ubbelohde viscometer. The intrinsic viscosity (g) was calculated from these measurements. The complex dynamic viscosities G' of the copolyester melts were recorded using a Rheometrics mechanical spectrometer RMS-605, operating in the dynamic shear mode between two parallel plates at 130 °C. The frequency was varied from 0.1 to 100 rad/s. The radius of the samples was 25 mm and the thickness was about 1.0 mm. The samples were prepared by press molding at 130 °C.

Table 2. Intrinsic viscosity data of random co-polyesters

Polymers	PPFCDC	PPFCDM	PCDMFCDC
Intrinsic viscosity, dL/g	0.52	0.50	0.63

One of the best known viscosity-molecular constitution relationship proposed by Dunstan is

$$\log \eta = aM + b \quad (1)$$

where η is viscosity, M is Molecular weight and a & b are constants. The constant a is for all homologous series and b is a constitutive factor characteristic of a particular series.

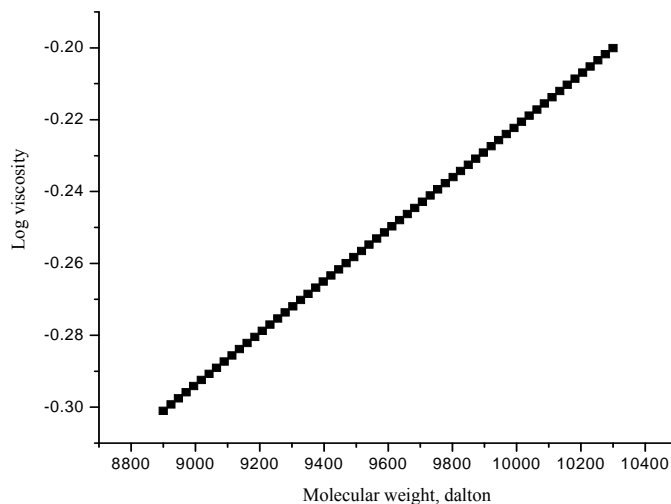


Figure 4. Shows the variation of viscosity *versus* molecular weight

From the graph (Figure 4) the value of ' a ' is calculated as 7.4×10^{-5} and the value of b is found to be -0.32. The constant value ' a ' refers to homologous series of esters and the value of ' b ' indicates the value of copolyesters of the particular compound pertaining to the present investigation.

Figure 5 and 6 show the variations of viscosity and molecular weight with three different copolyesters. General trend is increasing with three different copolyesters.

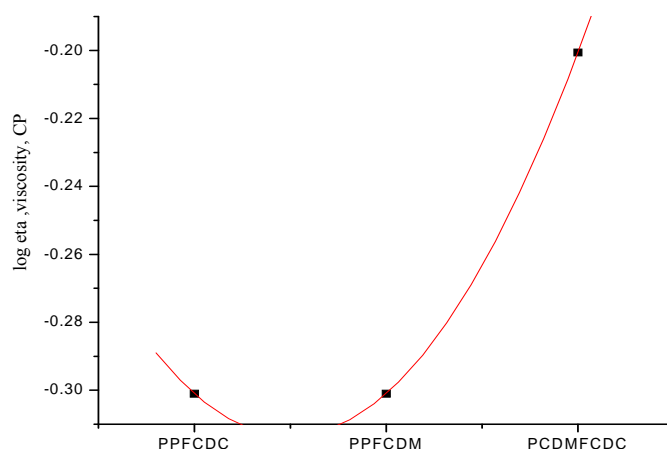


Figure 5. The variations of viscosity with three different copolyesters

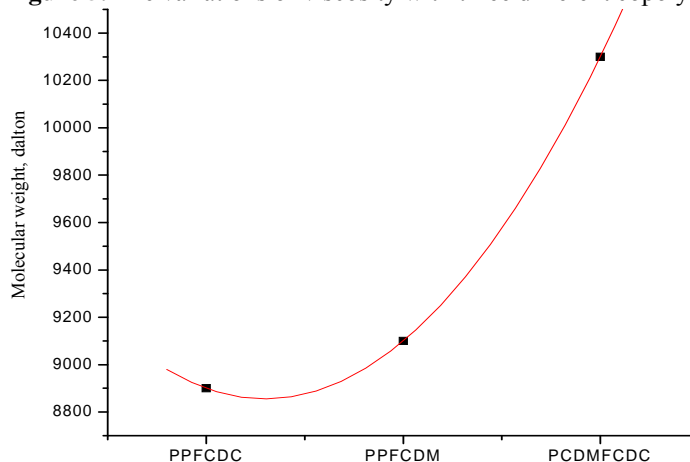


Figure 6. The variations of molecular weight with three different copolyesters

Solubility test

All the synthesised polymers were easily soluble in aprotic polar solvents like tetrahydrofuran, dimethyl sulphoxide, dimethyl formamide, dimethylacetamide, dioxane, and p-cresol and in chlorinated solvents such as methylene dichloride, chloroform and insoluble in toluene, *n*-hexane, benzene, xylene, diethyl ether and other hydrocarbons solvents. This may be due to the inter-molecular interactions of polar solvents with ester linkage of the polymer molecules. Some of the polymers do not dissolve in the above said solvents; which polymer does not dissolve, in which other solvent it is dissolving. This might be due to the high rigid aromatic nature of the polymers¹⁰⁻¹¹.

Solubility of copolymers was determined by dissolving 0.5 g of samples in 10 mL of chloroform or a trichloroacetic/chloroform mixed solvent at room temperature. The solubility is indicated by number of '+'. Essentially, the samples were first dissolved in chloroform. If a complete dissolution is achieved within 10 min at ambient temperature, solubility is rated as '+++'. If a complete dissolution is not achieved within 10 min at ambient temperature, solubility is rated as '++', '+', or '0'.

For samples taken longer time to completely dissolve in chloroform, the solubility was measured in a trichloroacetic acid/chloroform mixed solvent. The rating of ‘++’ and ‘+’ indicates that the samples are fully dissolved in 2% (w/w) and 5% of trichloroacetic acid/chloroform mixed solvent within 10 min, respectively.

Table 3. Solubility data of random copolyesters

S.No	Polymer	Acetone	CHCl ₃	DMSO	Pyridine	Methanol	Ethanol	Ethylacetate	THF	DMF	Water
1	PPFCDC	+++	+++	++	- +	--	+++	+++	++	- +	--
2	PPFCDM	+++	+++	++	- +	--	--	++	++	++	--
3	PCDMFCDC	+++	+++	++	- +	--	--	++	++	++	--

Conclusion

The MW-assisted synthesis of copolyesters from propanediol, 3-diol and 1, 4-cyclohexanedimethanol with various carboxylic acids in the presence of titanium isopropoxide as the catalyst was performed. In order to improve the thermal and mechanical properties of the poly(ester carbonate)s, chain-extension products (PCDMFCDC, PPFCDM and PPFCDC) were also synthesized starting from dihydroxy-terminated oligomers obtained by the etherification of succinic acid in the presence of 1,3-propanediol and 1,4-cyclohexanedimethanol (PCDMFCDC, PPFCDM and PPFCDC). Characterization of the molecular weight and branching index indicated that synthesis of long chain branched low T_g polyesters in the presence of mono functional reagents retarded gel formation and permitted synthesis of gel free polymers having higher degrees of branching, intrinsic viscosity data of random copolyesters, 0.52, 0.50 and 0.63.

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