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Poly(ethylene terephthalate) terpolyesters containing 1,4-cyclohexanedimethanol and isosorbide

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Introduction

Poly(ethylene terephthalate) (PET) is a thermoplastic polyester widely used in the field of textile and packaging industry [1,2]. However, due to its constitutional regularity it has a high tendency to crystallize which is an inconvenient for those applications in which a high transparency is required. To overcome this limitation, we have synthesized and characterized new terpolyesters derived from PET that incorporate varying amounts of 1,4-cyclohexanedimethanol (CHDM) and D-isosorbide, a biobased monomer.

Materials and methods

PECIsT terpolyesters were obtained by a two step melt polycondensation procedure, from terephthalic acid, ethylene glycol, and variable amounts of CHDM and isosorbide on a Karl Kurt Juchheim stainless steel reactor. The molecular weights were determined on a Waters GPC system. NMR spectra were recorded on a Bruker AMX-300 from samples dissolved in $CDCl_3$. Thermal properties were evaluated on a PerkinElmer DSC Pyris 1 calibrated with indium and zinc at heating/cooling rates of 10 $°C \cdot min^{-1}$ under nitrogen circulation. Termogravimetric analysis (TGA) were carried out on a PerkinElmer TGA-6 thermobalance at a heating rate of 10 $°C \cdot min^{-1}$ under a nitrogen atmosphere.

Results and discussion

The structure of PECIsT terpolyesters is shown in Figure 1. They were obtained with fairly high molecular weights and intrinsic viscosities ranged between 0.55-0.7 $dL \cdot g^{-1}$ (Table 1).

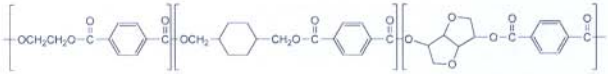

Figure 1: Chemical structure of PECIsT terpolyesters

The composition of the PECIsT terpolyesters, determined from ^1H NMR spectra showed that small amounts of isosorbide were lost in the polycondensation, and that all of them contain small amounts (less than 3%) of diethyleneglycol units as a consequence of the occurrence of etherification side reactions.

Table 1: Composition and molecular weights of PECIsT terpolyesters

Polyester	Final composition E/C/Is	Molecular weights			T_g (°C)
		$[\eta]$ ($dL \cdot g^{-1}$)	Mw ($g \cdot mol^{-1}$)	PD	
$PE_{70}C_{30}T$	71.4/28.6/0	0.70	32400	2.3	81
$PE_{70}C_{25}Is_5T$	73/23.4/3.6	0.64	30600	2.3	84
$PE_{70}C_{20}Is_{10}T$	74.3/19.2/6.5	0.63	30100	2.5	88
$PE_{70}C_{15}Is_{15}T$	75.6/14.4/10	0.61	25900	2.4	91
$PE_{70}Is_{30}T$	76.9/0/23.1	0.55	26600	2.4	105

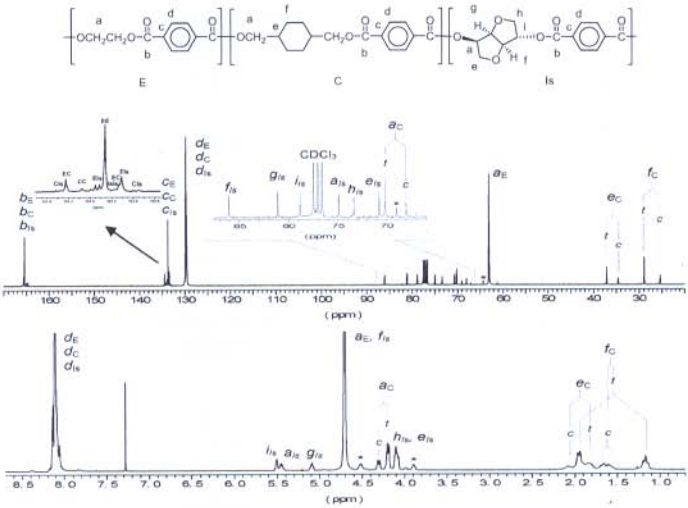

Figure 2: ^{1}H and ^{13}C NMR spectra of $PE_{70}C_{15}Is_{15}T$ terpolyester

Figure 2 shows both ^{1}H and ^{13}C NMR spectra of $PE_{70}C_{15}Is_{15}T$ with indication of peak assignments. Signals due to nonprotonated aromatic carbons showed splitting due to sequence effects at the level of dyads (left inset in Figure 2). By integration of these signals the number average sequence length and the degree of randomness were calculated. It was determined that all terpolyesters synthesized have a random distribution of comonomers in the polymer chain.

Finally the thermal properties were evaluated. Terpolyesters with 70 or 80 mol % of E units were observed to be almost amorphous for any content in C or Is units. Additionally it was observed that the T_g of the terpolyester increased with the content of Is units in the copolymer (Table 1). All terpolyesters showed good thermal stability as determined by TGA measurements.

Conclusion

New PET derived terpolyesters have been synthesized by incorporation of CHDM and the biobased monomer isosorbide. It was observed that this incorporation repressed the crystallinity, increased the T_g, improved the processability.

Acknowledgments

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References

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