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STEREO-ORDERED POLY(HYDROXYL ETHERS) BY CONDENSATION OF BISPHENOLS WITH DIGLYCEROL DICARBONATE

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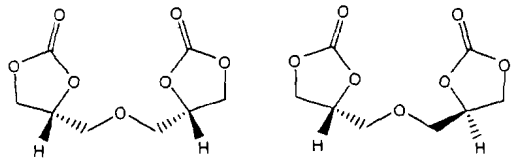
Introduction

Five-membered cyclocarbonates of glycerol are a remarkable class of compounds attracting research interest due to their potential use in the preparations of "green" chemicals and materials, e.g. solvents, surfactants, moisture insensitive nonisocyanate polyurethanes and other heterochain polymers.[1]

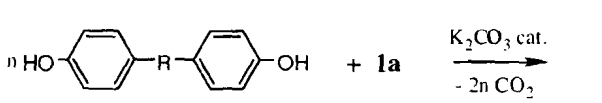
High molecular weight poly(hydroxyl ethers) [analogs of epoxy resins] of diphenols were previously synthesized by cyclic carbonate ring opening by potassium salts of diphenols at 70-90°C using simple glycerol derivatives.[2] The polymers were characterized by linear structure with a minimized amount of branches.

Our recent separation of the two diastereoisomers of diglycerol dicarbonate (**1a** and **1b**)[3] prompted us to undertake a study on the stereoselectivity of polycondensation of bisphenols **2** with **1a** (**1b**) to give the poly(hydroxyl ether)s **3a** (**3b**).



dl, **1a** meso, **1b**

α,α-diglycerol dicarbonate



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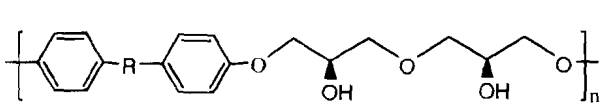

3a

Results

Reactions with bisphenol A were carried out in neat with catalytic amount (0.1-10%) of potassium carbonate at 130-200°C. Nearly stoichiometric amounts of carbon dioxide was evolved from the medium and a transparent colorless or light yellow glassy material was obtained by cooling the reaction mixture. Entirely alternating copolymers can be produced in this method with full conservation of stereochemistry at the hydroxyl groups, as deduced by ^{1}H-NMR analysis. Typical conditions used and yield observed are reported in Table 1, along with the main physical properties of crude and purified (by dioxane/water precipitation) polymers.

Polymers with high yield and having the highest molecular weight (M_v = 40.000) are obtained after 6 h polymerization.

Table 1. Polycondensation of bisphenol A (R = CMe_2) and diglycerol dicarbonates **1a** and **1b** and key properties of the obtained polymer.

1	[1]/[2]	cat. (%)	t (h)	Tg (°C)	$\overline{M}$ *
1a	0.41	10	1	n.a.	1000
1a	0.66	10	1	n.a.	2000
1a	0.74	10	1	n.a.	3000
1a	0.82	10	1	70	6000
1b	0.82	10	1	65	6000
1a	0.87	10	1	n.a.	12000
1a	0.91	10	1	n.a.	29000
1a	0.99	10	1	n.a.	38000
1a	0.99	1	0.5	n.a.	800
1a	0.99	1	1	n.a.	9000
1a	0.99	1	2	n.a.	18000
1a	0.99	1	3	n.a.	22000
1a	0.99	1	4	n.a.	24000
1a	0.99	1	5	n.a.	26000

*Molecular mass Deduced by ^{1}H-NMR analysis; n.a. = not available

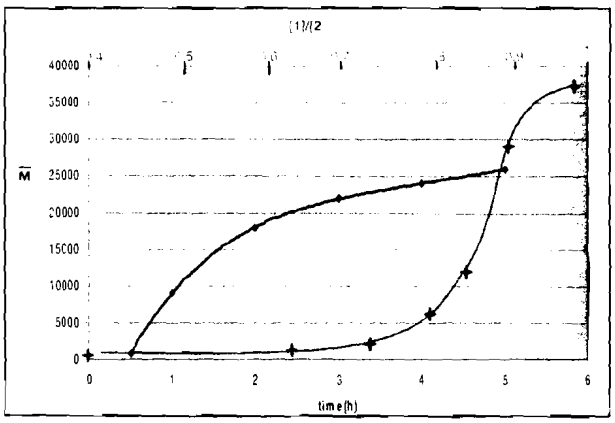

Figure 2. Effect of polymerization time (conditions: **1a/2**/K_2CO_3 1.1:1:10^{-2}) and monomer ratios (T = 180°C; h = 1.25; **1a**/K_2CO_3 1:0.1).

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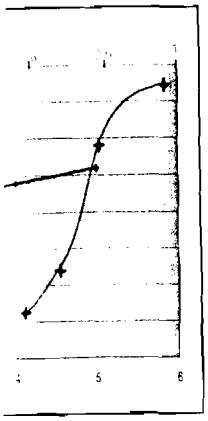
nd purified (by

ing the highest
btained after 6 h

ol A (R = CMe_2)
and key properties

Tg (°C)	$\overline{M}$ *
n.a.	1000
n.a.	2000
n.a.	3000
70	6000
65	6000
n.a.	12000
n.a.	29000
n.a.	38000
n.a.	800
n.a.	9000
n.a.	18000
n.a.	22000
n.a.	24000
n.a.	26000

analysis; n.a. = not



n time (conditions:
r ratios (T = 180°C;

Differential scanning calorimetry (DSC) analysis revealed that polymers **3a** and **3b** is completely amorphous. DSC traces clearly showed a glass transition with an enthalpic relaxation phenomenon. In the first scan (from -25°C to 250°C at 10°C as heating rate) the glass transition temperature (Tg) was detected at about 53°C and a remarkable enthalpic relaxation was observed. In the second scan (under the same experimental conditions) a Tg at about 65°C and a minor enthalpic relaxation were detected.

Conclusions

Stereoisomeric poly(hydroxyl ether)s are a promising next generation materials with high chemical resistance and good adhesion and mechanical properties. Using the appropriate diphenols, these polymers are environmentally friendly and do not consist of any dangerous components. Moreover, they can be further functionalysed at the hydroxyl functional groups and the stereoselectivity potential is under screening.

Acknowledgment

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