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Microwave-assisted synthesis of polyesters containing 1,4:3,6-dianhydrohexitols.

Abstract

Series of reactions were carried out for three dianhydrohexitols (isosorbide, isomannide and isoidide) and one aliphatic carboxylic acid – suberic acid - and its derivatives. The reactions were performed in the microwave reactor in an open vessel equipped with mechanical stirrer. Polymer products with highest yields were obtained in reaction of isosorbide and suberoyl chloride. For microwave reactions with the most satisfactory yields, conventional synthesis were also performed.

Keywords: polyesters, dianhydrohexitols, microwave

Introduction

Dianhydrohexitols are interesting family of bifunctional monomers which are: 1,4:3,6-Dianhydro-D-glucitol (isosorbide), 1,4:3,6-Dianhydro-D-mannitol (isomannide), 1,4:3,6-Dianhydro-D-iditol (isoidide). Isosorbide is easily received on the industrial scale by double dehydratation of D-glucose [1,2], isomannide is prepared by dehydratation of mannitol.
They have been used in synthesis of polymers as: polycarbonates, polyurethanes, polyethers and polyesters.
Polyesters based on isoidide, isomannide and terephthaloyl chloride were synthesized by Thiem et al. [3] without solvent. The same polyesters but of higher molecular weight, were synthesized in solution [4]. Problem in this type of reaction is HCl, which causes degradation of polymer molecules and decreases molecular mass. Some solution is conducting reaction in solvent – pyridine [4].
More recently, Okada et al. synthesised series of polyesters on the base of 1,4:3,6-dianhydrohexitols and acid chlorides of dicarboxylic acids $ClCO(CH_2)_nCOCl$, where n=2-10. They were degradable by enzymes, in soil and in presence of phosporus buffer[5-8]. Methyl esters of relative acids were also used for synthesis [8].
Polyesters based on aromatic acids, such as terephtaloyl chloride and 2,5-furandicarboxylic acid chloride, are characterized by good thermal properties [4,9,10].
So far, the microwave irradiation was applied to synthesis of new diols of dianhydrohexitols, afterwards for the synthesis of polyeters based on this diols [11-16].
In case of polyesters synthesis, we have already succeed in microwave-assisted synthesis of unsaturated polyesters from acid anhydrides and different diols [17]. We also tried to incorporate isosorbide to the structure of unsaturated polyester [18].

Experimental part

Dianhydrohexitols were obtained from Société Roquette-Frères; isosorbide and isomannide were recrystallized from acetone, isoidide was used as received; suberic acid and thionyl chloride was purchased from Acros Organics.
Suberoyl chloride was obtained via reaction of suberic acid with thionyl chloride.
Suberic acid dimethyl ester was obtained via reaction of suberic acid in methanol and purified by multiple extraction with water.

For the microwave synthesis Prolabo Synthewave 402 reactor, with an open vessel and mechanical stirring, was used. FISO optical fiber served to control the reaction temperature during the reactions. In conventional synthesis oil bath equipped with temperature control was used. If it is not mentioned, reaction time was always 60 min.

Polymers were precipitated in mixture of chloroform and methanol and dried, then polymer yields were calculated. If yields were satisfactory, reactions were made also under conventional conditions.

GPC analysis was done for products soluble in THF, if not, only melting points were determined.

Results and discussion

Results of microwave reactions of isosorbide with suberic acid in solution are presented in Table 1. Acidic catalyst initiates reaction but together degrades polymer; optimal amount of catalyst was maintained as 1.0% by wt.

Table 1.

Solvent	H_2SO_4 [% by wt]	Temperature [°C]	Polymer yield [%]	M_n	M_w	P_d
Toluene	0.5	130	No polymer	-	-	-
Toluene	1.0	130	51	2459	3481	1.4
Toluene	5.0	150	10	2701	4080	1.5
Xylene	1.0	150	44	3463	4581	1.3
Xylene	5.0	150	No polymer	-	-	-

No polymer was obtained in conventional reaction (1%by wt H_2SO_4,130^{o}C, 60min.)

Results of microwave reactions of isosorbide with suberic acid dimethyl ester are presented in Table 2. In this case we have used different groups of catalysts, but still no polymer was obtained anywise. As acidic catalyst were used suberic acid (0.01M/M of suberic acid methyl ester) and sulphuric acid. As base: potassium carbonate with and without presence of methanol; sodium methoxide. As PTC: Aliquat 336.

Table 2.

Catalyst [% by wt]	Temperature [^{o}C]	Polymer yield [%]
$HOOCCH_2(CH_2)_4CH_2COOH$	130	No polymer
K_2CO_3, 10% by wt of isosorbide	130	
K_2CO_3 10% by wt of isosorbide, MeOH	130	
H_2SO_4, 1.0%	130	
H_2SO_4, 5.0%	130	
Aliquat 336, 10% by wt of isosorbide	130	
MeONa, by wt of isosorbide	130	

Conventional reaction in presence of 1% H_2SO_4, 12h, polymer yield 20%

Results of microwave and conventional reactions of isosorbide and suberoyl chloride in bulk and solution are presented in Table 3. In that reaction, the best yields of polyester with considerable highest molecular masses were obtained in solvent reaction (toluene) at temperature 110^{o}C.
To avoid hydrogen chloride negative effect, some amount of pyridine was added (1.5M/M HCl). We expected of improvement of polymer properties, nevertheless, polydyspersity increased, probably because of by-side reactions of pyridine (microwave reaction in mixture of pyridine and toluene in temperature 110^{o}C, polymer yield 9%).
We also tried to use more polar solvent for reactions at higher temperature (NMP). In temperature of 200^{o}C polymers were obtained with satisfactory yield (Y=76%) after 10 minutes.

Table 3.

Solvent	Temperature [^{o}C]	Polymer yield [%]	M_n	M_w	P_d
-	80	58 (40)	4287 (3905)	7911 (5883)	1.9 (1.5)
-	130	41 (49)	2645 (2557)	5462 (4730)	2.1 (1.9)
Toluene	110	79 (79)	13550 (10090)	17200 (13830)	1.3 (1.4)
Toluene /Pyridine	80	40 (30)	9275 (6123)	12860 (10310)	1.4 (1.7)
Toluene /Pyridine	110	9 (44)	4627 (9622)	10520 (13860)	2.3 (1.40)
NMP	150	47 (52)	4536 (3579)	6643 (5292)	1.5 (1.5)
NMP	200,10’	76	6530	10390	1.6

In brackets results of conventional reactions

Results of microwave and conventional reactions of isomannide and suberoyl chloride in bulk and solution are presented in Table 4. In this case, we obtained better results in solventless conditions.

Table 4.

Methods	Solvent	Temperature [^{o}C]	Polymer yield [%]	Mn	Mw	Pd
MW	-	80	89 78	6457 (9383)	10650 (12570)	1.7 (1.8)
MW	-	110	63 52	13230 (14930)	16790 (18320)	1.3 (1.2)
MW	Toluene	110	18 26	8849 (8910)	11460 (13290)	1.3 (1.5)

In brackets results of conventional reactions

Results of microwave and conventional reactions of isoidide and suberoyl chloride in melt and in solution are presented in Table 5.

Table 5.

Methods	Solvent	Temperature [^{o}C]	Polymer yield [%]	Mp [^{o}C]
MW	Toluene	110	65 (74)	142 (146)
MW	Toluene	130	69 (72)	142 (144)

In brackets results of conventional reactions

Generally, yields and molecular weights of polymer were similar with both (microwave and conventional) methods. The only exception was the reaction of isosorbide and suberic acid in the presence of catalytic amount of sulfuric acid. In this case under conventional conditions we didn't obtain polymer at all.

Only two of three ways to obtain polyester via polycondensation reaction worked. Our attempts to obtain polymer via reaction of dimethyl ester of suberic acid and isosorbide were useless, despite using different catalytic systems (methyl esters of dicarboxylic acids were used by Okada et al. [8]).

In reaction of suberic acid and isosorbide in the presence of catalytic amounts of sulfuric acid we obtained black polymers. Bulk polycondensation of suberoyl chloride and isosorbide led to colourless polymers. By addition of solvent (toluene) to this reaction we obtained polymers with higher molecular masses.

Reaction of isomannide and suberoyl chloride led to black polymers with relatively higher molecular masses (ca. 10 000).

Reaction of isoidide and suberoyl chloride led to white polymers with high melting point (mp≈150^{o}C).

Conclusion

Series of polyesters based on 1:4,3:6-dianhydrohexitols and suberic acid moieties were successfully synthesized under microwave conditions:

-molecular weights of polymers based on isosorbide varied from 2000 to 10 000, while polymer yields varied from 9 to 80%

-molecular weights of polymers based on isomannide varied from 6 000 to 18 000, and polymer yields varied from 18 to 89%.

-molecular weights of polymers based on isoidide were not determined since they are not soluble in THF. In this case yields of polymers varied from 65 to 72%.

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