

Synthesis and Spectroscopic Analyses of New Polycarbonates Based on Bisphenol a-Free Components

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S2.3 Synthesis of monomers

S2.3.1 Synthesis of 1,1'-methanediylbis[1-(chloromethyl)benzene]

225g (1.33 mol) of diphenylmethane, 92g (1.02 mol) of **paraformaldehyde**, 320g (2.24 mol) of anhydrous 98% zinc chloride and 320 cm³ of pure acetic acid, 140 cm³ of concentrated 36% hydrochloric acid and 400 cm³ of cyclohexane were added, and then while stirring, gaseous hydrogen chloride was added at such a rate that the temperature of the mixture increased by 0.5°C for a minute. Under these conditions, the contents of the flask turned transparent after about 2 hours and reached a temperature of about 50°C. The further course of the reaction did not provide enough heat to maintain this temperature, so hydrogen chloride was passed through while heating the contents of the flask in a water bath at 57–62°C. After 3 hours the reaction was completed and after stopping the flow of hydrogen chloride, the flask contents split into two liquid phases, the upper, lighter, main product having the appearance of a greenish oil. After cooling the contents of the flask to room temperature, the layer was easy to filter. After the mass was filtered off, washed with water and compressed, there was obtained a crude product which was washed twice with 5% Na₂CO₃ solution, 500 cm³ each, and twice with methanol, 160 cm³ each. 160g of product was obtained.

S2.3.2 Synthesis of (methanediyl)dibenzene-4,1-diyl)dimethanethiol (Ditiol)

In a 1000 cm³ round bottom flask, 122g (0.46 mol) of 1,1'-methanediylbis[4-(chloromethyl)benzene] was dissolved in 450 cm³ of 1,4-dioxane and after the addition of 71g (0.93 mol) of thiourea at a reflux for 1 hour. The isolated precipitate of the isothiurea salt was filtered off cold. 800 cm³ of a 12% aqueous NaOH solution was added and refluxed for 1 hour under a water-jacketed reflux condenser. The solution was filtered hot and the cooled filtrate acidified with dilute hydrochloric acid (1:1). A fine crystalline precipitate separated from the solution left at room temperature was filtered off, and then purified by dissolving 10% aqueous NaOH twice in 800 cm³ and precipitating with the 5% HCl solution. The crude product was purified by crystallization from ethanol (1g per 10 cm³ of the solvent).

S2.3.3 Synthesis of 2,2'-[methanediylbis(benzene-4,1-diylmethanediyl)sulfanediyl]diethanol (Diol E)

30g (0.12 mol) of dithiol was dissolved in 500 cm³ of a 10% aqueous NaOH solution, then the solution was transferred to a 1000 cm³ three-necked flask equipped with a mechanical stirrer, water jacket reflux condenser and dropping funnel. 20.33g (0.25 mol) of 2-chloroethanol was added via a dropping funnel. As the reaction proceeded, a white precipitate of diol E appeared. The dropping funnel was washed with 10 cm³ of ethanol. The whole was heated in a boiling water bath for 1.5 h. After cooling, the separated precipitate was filtered off on a funnel and washed with distilled water until becoming neutral. The crude product was purified by recrystallization twice from benzene (120 cm³). 26g of diol E was obtained.

Citation: Wnuczek, K.; Puszka, A.; Podkościelna, B. Synthesis and Spectroscopic Analyses of New Polycarbonates Based on Bisphenol A-Free Components. *Polymers* **2021**, *13*, 4437. <https://doi.org/10.3390/polym13244437>

Academic Editors: Andrzej Puszka, Beata Podkościelna and Dan Rosu

Received: 19 November 2021

Accepted: 13 December 2021

Published: 17 December 2021

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S2.3.4 Synthesis of 6,6'-(methanediyl(benzene-4,1-diylmethanediylsulfanediyl)dihexan-1-ol (Diol H)

30g (0.12 mol) of dithiol was dissolved in 500 cm³ of a 10% aqueous NaOH solution, then the solution was transferred to a 1000 cm³ three-necked flask equipped with a mechanical stirrer, water jacket reflux condenser and dropping funnel. Using a dropping funnel, 35.95g (0.25 mol) of 6-chlorohexan-1-ol was added in small portions. As the reaction progressed, a white precipitate of diol H appeared. After the dropwise addition, the funnel was washed with 10 cm³ of ethanol, and then the contents of the flask were heated in a boiling water bath for 1.5h. After cooling, the contents of the flask with the separated product were filtered on a funnel, washed with distilled water until becoming neutral and dried. The crude product was crystallized from benzene (150 cm³) to obtain 50g of diol H.

S.3 Results and discussion

S3.2 ATR-FTIR analysis

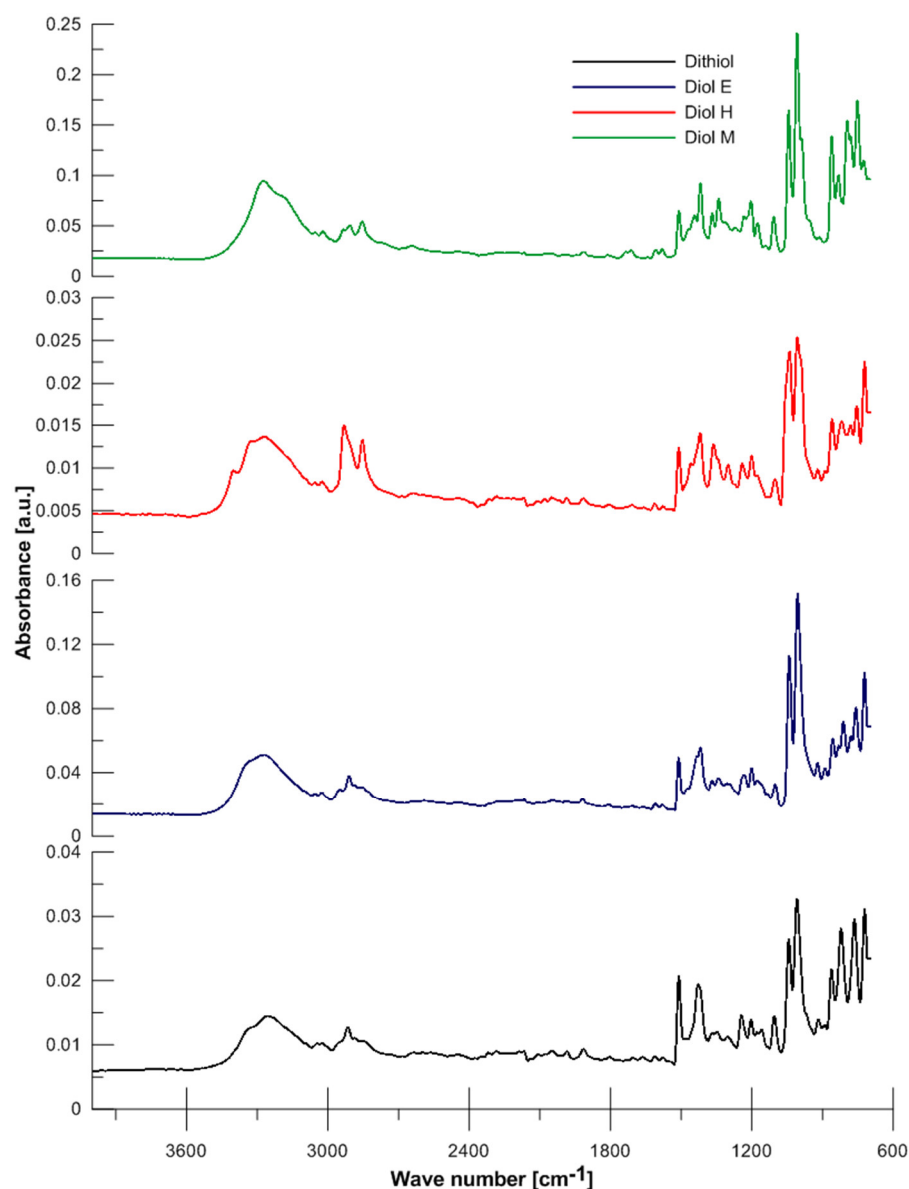


Figure S1. ATR-FTIR analyses of monomers.

Table S1. Characteristic signals on ATR-FTIR spectra of monomers [cm⁻¹].

Monomer	-OH	Ar-H	-CH ₂ -	-C-H-	-C-O-	C-C-	R-Ar-R	-S-CH ₂ -
Dithiol	-	3256	2915	1203	1105	1243	1509	1427
		3023	1368		1043		861	1008
		1914					762	917
		721						
Diol E	3270	889	721	110	1039	811	758	920
		1510	1417	1200	1234			1005
		2910		1312	1340			
Diol H	3269	858	721	1100	1041	818	780	1006
		1510	1419	1200	1240			2853
		2931		1300	1362			
Diol M	3274	3021	2906	2853	1043	1175	795	-
		860	725	1203	1107		751	
				1007	1340			
					1368			
					1417			