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New Aliphatic Polymalonamides

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New Aliphatic Polymalonamides

by

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Abstract

New aliphatic polymalonamides were synthesized by interfacial polymerization and bulk polymerization using phenyl esters. Polymers obtained by bulk polymerization revealed higher inherent viscosities than those obtained by interfacial polymerization. Films of several polymers were made by melt procedures. By DSC, only 7-3 polymalonamide was crystalline.

Introduction

Although many aliphatic AABB polyamides have been synthesized, polymalonamides have been neglected. The only references we have found are in the patent literature. Carother's original patent on polyamides presented several examples based on diethyl malonate.[1] Subsequently, Floyd reported polymerizations of aliphatic diamines with malonate esters, and Speck described the advantageous use of diphenyl malonates.[3]

In another connection, we were interested in aliphatic polymalonamides and have investigated their synthesis.

Results

We have carried out interfacial polymerizations using diacid dichlorides and also bulk polymerizations using diphenyl esters.

Interfacial Polycondensations. Table I presents our results. Using four different aliphatic diamines, high polymers have been obtained from diethyl or ethylmalonyl dichloride. Yields were high, ranging from 97.6%-99.5%

Bulk Polymerization. Table II present our results. Diphenyl diethylmalonate underwent successful polycondensation with four aliphatic diamines, while

diphenyl malonate condensed successfully with 1,7-diaminoheptane. Yields were quantitative and the inherent viscosities were significantly higher than those obtained by interfacial polycondensation.

Polymer Properties. Regardless of the synthesis route, these polyamides displayed surprisingly little tendency to crystallize. Only the 7-3 polyamide from 1,7-diaminoheptane and diphenyl malonate could be crystallized, DSC m.p. 220°C.

Solubilities. The 7-3 polymalonamide did not dissolve in acetone, cyclohexanone, acetonitrile or chloroform, but the other polymers were soluble in these solvents. The difference of the solubilities was related to the crystallinity of the polymers.

Film Formation - The 7-3 polymalonamide gave brittle films from trifluoroacetic acid. Melt procedures of several of the other polymers also gave films. Table I and II show the temperature at which film strips became mobile, but orientation, as indicated by "necking-down," on drawing was not observed.

Discussion

We have synthesized a number of new aliphatic polymalonamides in high yields and reasonable molecular weights. Bulk polycondensation gave appreciably higher molecular weights than interfacial polymerization, possibly because malonyl dichlorides are expected to hydrolyze rapidly.

Despite the high fraction of CONH groups in these polymers, they generally remained noncrystalline. Only the unhindered 7-3 polymer packed well enough to allow crystallization.

Experimental

Materials

Diethylmalonyl dichloride, adipoyl chloride, 1,3-diaminopropane, 1,5-diaminopentane, 1.7-diaminoheptane, 1.9-diaminononane and hexamethylenediamine were obtained from Aldrich and purified by distillation. Diphenyl adipate,[4] ethylmalonyl dichloride[5] and diphenyl malonate[6] were synthesized and purified by distillation.

Synthesis of Diphenyl-1,1-diethylmalonate

Diethylmalonyl dichloride (15g 76.1 mmol) and phenol (15.7g, 167 mmol) were placed in a 250 mL three-necked flask with condenser and heated at 200°C for 3 h. The mixture was cooled to room temperature and kept at room temperature for 48 h. Then it was heated at 200°C for 1 h and at 60°C for 1 h at 30 mmHg, to obtain complete removal of HCl. The product was distilled twice under vacuum. Diphenyl-2,2-diethylmalonate boiled at 168.0-173.0°C/0.25 mmHg. The yield was 70.0%. ^{1}H NMR ($CDCl_3$): 1.02 (t, 6H), 2.22 (q, 4H), 7.32 (m 10H) ppm IR (KBr) 3063, 2974, 1747, 1589, 1186 cm^{-1} Anal. Calcd. C 73.08, H 6.41, O 20.51, Found C 73.12, H 6.38, O 20.50.

Polymerization

Interfacial Polycondensation

In 100 mL blender, a solution of diamine (5 mmol) and sodium hydroxide (11 mmol) was placed in 20 mL of water. The solution was cooled in an ice bath. The blender was turned to high speed. A solution of acid chloride (5 mmol) and 20 mL of chloroform at 0°C was added into the blender. After the addition, the mixture was stirred for 2 min. The polymer was collected on a glass filter and washed with water until free of alkali and salt. The polymer

was dried under vacuum. Yield: 97.6-99.5%

Bulk Polycondensation

A carefully weighed mixture of phenyl ester (5 mmol) and diamine (5 mmol) was placed in a polymerization tube, which was then evacuated and filled with nitrogen. The tube was sealed and heated for 18 h. at 140-200°C in an oil bath. The temperature depended on the boiling temperature of diamine. The tube was opened and fitted with a nitrogen capillary bleed reaching to the bottom of the tube. The tube was then heated for 2 h. at 260°C in an oil bath at atmospheric pressure and finally for 4 h under vacuum, with a slow stream of nitrogen passing through the melt. The tube was cooled to room temperature, then opened and the glass broken away from the polymer. Except for mechanical losses in isolation, the yields were quantitative.

Measurement of Inherent Viscosity

A polymer was dissolved in m-cresol. The concentration was about 2%. The inherent viscosity was measured at 30°C.

Measurement of Film Drawing Temperature and Stickiness Temperature

A melt-cast film of a polymer was made using a Carver Laboratory Press. The film was cutting to a 5 mm x 10 mm strip. The strip was put on a Kofler Heizbank and the film drawing temperature and the stickiness temperature were determined.

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Table I Interfacial Polycondensation

Run	Monomer A	Monomer B	ηinh (dL/g)	Film Drawing Temp.(°C)	Stickiness Temp.(°C)
1	Diethylmalonyl chloride	1,3-Diaminopropane	0.17	--	--
2	"	1,5-Diaminopentane	0.40	70	118
3	"	1,7-Diaminoheptane	0.35	--	--
4	"	1,9-Diaminononane	0.19	--	--
5	Ethylmalonyl chloride	1,3-Diaminopropane	0.44	--	--
6	"	1,5-Diaminopentane	0.45	--	--
7	"	1,7-Diaminoheptane	0.44	85	85
8	"	1,9-Diaminononane	0.45	--	--
9	Malonyl chloride	1,7-Diaminoheptane	0.18	--	--
10	Adipoyl chloride	Hexamethylenediamine	0.93	--	--

Table II Bulk Polycondensation

Run	Monomer A	Monomer B	ηinh (dL/g)	Film Drawing Temp.(°C)	Stickiness Temp.(°C)
1	Diphenyl 1,1-diethyl-malonate	1,3-Diaminopropane	0.44	90	110
2	"	1,5-Diaminopentane	0.57	74	92
3	"	1,7-Diaminoheptane	0.65	56	86
4	"	1,9-Diaminononane	0.52	40	78
5	"	1,5-Diaminopentane	0.51	--	--
6	"	"	0.60	78	94
7	"	1,7-Diaminoheptane	0.62	--	--
8	Diphenyl malonate	1,7-Diaminoheptane	0.67	72	72
9	"	"	0.61	--	--
10	Diphenyl adipate	Hexamethylenediamine	0.95	--	--

Run 5 The polymerization temperature at vacuum was 265°C. The color of the polymer turned to black.
6 The polymerization time at vacuum was 9 h.
7 Dibutyltin diacetate (0.015 mmol) was used as catalyst.
9 The polymerization temperatures under N_2 and vacuum were 200°C.

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