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Synthesis of Some Fumaric Acid Polyamides from Active Diester Monomers

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SUMMARY

The solution polycondensation of two active diesters, bis(2,4-dinitrophenyl) fumarate and 1,1'-(fumaroyldioxy)bis(benzotriazole), with a series of alphatic and aromatic diamines in N-methyl pyrolidone at room temperature, was investigated. The polycondensation reactions yielded a series of fumaric acids polyamides. The polymers obtained from aliphatic diamines were soluble in trifluroacetic acid and exhibited well-defined melting points. The polymers obtained from aromatic diamines are infusible at temperatures below 300°C but were thermally stable and soluble in dimethylacetamide containing 4% LiCl.

INTRODUCTION

The present study on the synthesis of fumaric acid polyamides was undertaken as a part of a study of the relationship between the macromolecular structure and rheological behavior of polymers. Special attention was given in this study to the influence of the cis/trans properties of these and related polymers. In general, polymers with cis units exhibit lower glass transition and melting temperatures than the corresponding trans polymers[1]. The polymers of the present study are of particular interest because they belong to the important class of thermoset resins referred to as "unsaturated polyesters", which are primarily low molecular weight copolyesters of fumaric, maleic and unsaturated acids[2].

In order to prepare polymers from maleic acid derivatives and to retain the cis configuration of this unit it is necessary to avoid high reaction temperatures which would cause isomerization of the cis double bonds into the more stable trans configuration. Acid chloride monomers are generally used for low temperature polycondensations, but maleic acid dichloride has never been prepared and reported, so we chose to use active ester derivatives of the monomer for the attempted preparation of high molecular weight polymers in aprotic solvents at room temperature. This method has been successfully used to prepare polyamides from the reaction of piperazine with sterically hindered dicarboxylic acids[4-6].

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EXPERIMENTAL

Synthesis of Active Diester Monomers

Bis(2,4-Dinitrophenyl)Fumarate (BDPF). To a solution of 18.41 g (0.1 mole) of 2,4-dinitrophenol and 10.22 g of triethylamine in 200 ml of THF was added dropwise 7.56 g (0.05 mole) of fumaric acid dichloride with stirring at room temperature. After stirring for 60 min. at room temperature, the reaction mixture was poured into 200 ml of water and the resulting precipitate was collected by filtration and dried in air. The crude product was recrystallized from acetone and again dried in air at room temperature. The yield was 14 g (62.5%); mp 195-198°C. Infrared (KBr): 1755 $cm^{-1}(\nu_{C=O})$ and 945 $cm^{-1}(\nu_{C=C})$. Anal. calculated for $C_{16}H_8H_4O_{12}$: C,42.86%; H, 1.76%; N, 12.5%. Found: C, 42.84%; H, 1.95%; N, 12.99%.

1,1'-(Fumaroyldioxy)bis(benzotriazole)(FBBT). To a solution of 13.51 g (0.1 mole) of 1-hydroxybenzotriazole and 10.22 g of triethylamine in 200 ml of THF was added dropwise 7.65 g (0.05 mole) of fumaric acid dichloride, and the mixture was stirred at room temperature for 60 min. The reaction mixture was then poured into 200 ml of water. The product which precipitated was isolated by filtration, washed with boiling ethanol and dried. The yield was 17.4 g (99.4%); infrared (KBr); 1755 $cm^{-1}(\nu_{C=O})$ and 985 $cm^{-1}(\nu_{C=C})$. Anal. calculated for $C_{16}H_{10}N_6O_4$: C, 54.86%; H, 2.85%; N, 24.00%. Found: C, 54.39%; H, 3.05%; N, 22.51%, C, 54.24%; H, 3.58%; N, 23.24%.

Synthesis of Polyamides

Diamines.- Aliphatic diamines, ethylenediamine (EDA), hexamethylenediamine (HMDA), octamethylenediamine (OMDA), dodecamethylenediamine (DDMDA), N,N'-dimethylhexamethylenediamine (DMHMDA) and piperazine (PIP), were reagent-grade and used as supplied by Fluker AG. Aromatic diamines also obtained from Fluker AG were purified by recrystallization; m-phenylenediamine (m-PDA), p-phenylenediamine (p-PDA) and 4,4'-diaminodiphenyl (DAB) from ethanol; bis(4-aminophenyl)methane (BAPM) from benzene; bis(4-aminophenyl)ether (BAPE) from tetrahydrofuran.

Solvent and Reagent: N-methyl-2-pyrolidone (NMP), was purified by vacuum distillation and stored over molecular sieves (4Å). Triethylamine (TEA) was reagent-grade and used without further purification.

Typical examples of the polycondensation of HMDA with each of two active diesters are given below. Polycondensations with other diamines were performed in an analogous way and are not separately described.

Polyamide from HMDA and BDPF. - To a solution of 1.12 g (0.0025 mole) of BDPF in 7 ml of NMP was added 0.29 g (0.0025 mole) of HMDA, and the mixture was stirred at room temperature for 24 hrs. The reaction mixture was then poured into 500 ml of a 1% sodium hydroxide water solution. The yellow precipitate was collected by filtration and thoroughly washed with water and boiling methanol. After drying at 100°C the polymer weighed 0.47 g (96%). Infrared (KBr): 3280 $cm^{-1}(\nu_{N-H})$; 1620 $cm^{-1}(\nu_{C=O})$; 990 $cm^{-1}(\nu_{C=C})$. The inherent viscosity was 0.51 dl/g.

Polyamide from HMDA and FBBT.- A solution of 1.75 g (0.005 mole) of FBBT and 0.58 g (0.005 mole) HMDA in 15 ml NMP was stirred at room temperature for 24 hrs. The mixture was poured into 1000 ml of hot water. The precipitate was repeatedly washed with hot water and then dried at 100°C. The yield was 0.75 g (77%). Infrared: 3280 $cm^{-1}(\nu_{N-H})$; 1625 $cm^{-1}(\nu_{C=O})$; 985 $cm^{-1}(\nu_{C=C})$. The inherent viscosity was 1.22 dl/g.

Polymer Characterization

Inherent viscosity was measured in a 96% sulfuric acid solution at 0.5 g/dl and 30°C.

Proton NMR spectra were recorded using a Perkin-Elmer instrument R 32 (90 MHz). Active diester was dissolved in deuterated dimethylsulfoxide using tetramethylsilane for reference signal. Polyamides from aliphatic diamines were dissolved in deuterated trifluoroacetic acid aided by hexamethyldisiloxane as a standard reference.

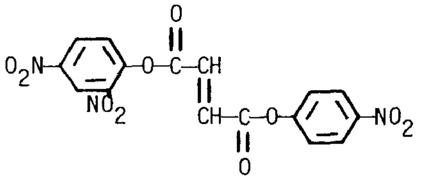
DSC measurements were made with a Perkin-Elmer instrument 2B in nitrogen, at a rate of 20°C/min.

TGA measurements were performed using a DuPont balance in nitrogen, at a rate of 20°C/min.

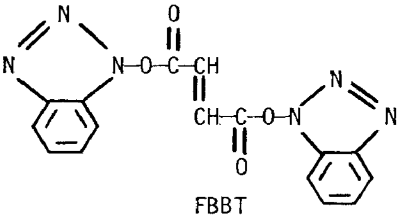
RESULTS AND DISCUSSION

Active Ester Monomers

Fumaric acid active diesters of 2,4-dinitrophenol (BDPF) and of 1-hydroxybenzotriazole (FBBT), shown below, were prepared in high yield by reacting 1 mole of the acid dichloride with 2 moles of the hydroxyl containing precursor in the presence of 2 moles of triethylamine in THF at room temperature. Their structure was confirmed by elemental analysis and infrared spectroscopy. In addition, the exclusively trans configuration of the double bonds in BDPF was demonstrated with proton NMR spectroscopy by the presence of a single peak at 6.68 ppm, which is characteristic for the protons on trans double bonds. For fumaric acid this peak is at 6.66 ppm while for malec acid the peak is at 6.64 ppm.



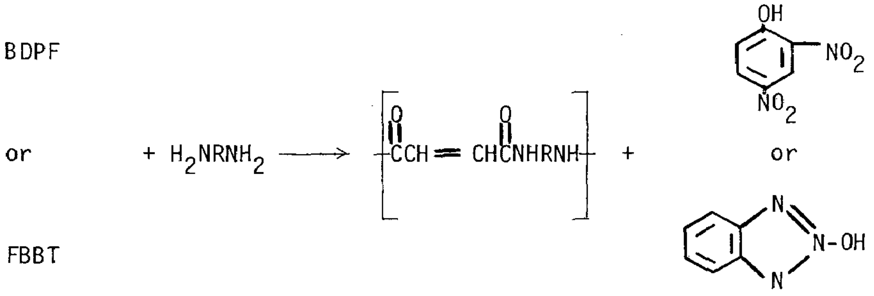
BDPF



FBBT

Polymerizations

Both fumaric acid active diesters, BDPF and FBBT, reacted readily with equimolar quantities of aliphatic and aromatic diamines in NMP at room temperature as shown in the following equation:



The yields of the fumaric acid polyamides derived from primary amines were almost quantitative, in contrast to those from secondary amines as shown in Table I. The inherent viscosities of these polyamides were reasonably high, but no clear correlation is apparent between monomer structure and inherent viscosity of the polymers (Table I).

There is a fair agreement between values for nitrogen content found by elemental analysis and calculated for polymer repeating units. (Table I). The infrared absorption spectra of all prepared polyamides exhibited a band of 965 to 985 cm^{-1} characteristic for fumaric acid double bonds. The carbonyl band at 3280 cm^{-1} for all polymers except for Polymer 10, where it occurred at 3260 cm^{-1}, and Polymers 6 and 7 which were not characterized, and N-H bending bands at 1495 to 1550 cm^{-1} were present in the spectra of polyamides from primary amines.

The proton NMR spectra were recorded for polyamides from aliphatic diamines, which are soluble in trifluoroacetic acid. The singlet peak for the protons on the trans double bond was present in all spectra at 6.68 to 7.18 ppm (Table I). The signals of other protons could also be identified. The areas below those signals were proportional to the numbers of corresponding hydrogen atoms in the polymer repeating units.

TABLE I

Polycondensation of Active Ester Fumarate Monomers with Diamines

	Monomers		Polymers				
Polymer	Diamine[b]	Diester[c]	Yield %	η_{inh}, dl/g	Nitrogen,% Calcd.	Nitrogen,% Found	^{1}H NMR ppm
1	EDA	BDPF	99	0.29	20.00	18.32	6.68
2	HMDA	BDPF	96	0.51	14.29	14.30	6.77
3	HMDA	FBBT	77	1.22	14.29	13.56	6.81
4	OMDA	BDPF	94	0.48	12.49	13.02	-
5	DDMDA	BDPF	96	0.40	9.99	10.19	-
6	DMHMDA	BDPF	65	0.28	12.50	11.66	7.12
7	DMHMDA	FBBT	38	-	12.50	11.05	7.11
8	PIP	BDPF	12	0.16	16.86	14.46	7.18
9	PIP	FBBT	23	0.16	16.86	17.76	-[a]
10	m-PDA	BDPF	98	0.27	14.89	14.15	-[a]
11	p-PDA	BDPF	98	0.30	14.89	14.18	-[a]
12	DAB	BDPF	98	0.41	10.61	10.07	-[a]
13	BAPM	BDPF	99	0.80	10.07	9.84	-[a]
14	BAPE	BDPF	99	0.97	10.00	10.19	-[a]

[a] NMR analysis not obtained as polymers were insoluble

[b] EDA-ethylenediamine. HMDA - hexamethylenediamine; OMDA - octamethylenediamine; DDMA - dodecamethylenediamine; DMHMDA - N,N'-dimethylenehexamethylenediamine; PIP - piperazine;; m-PDA-*m*-phenylenediamine; p-PDA-*p*-phenylenediamine; DAB - 4,4'-diaminiobiphenyl; BAPM - *bis*(4-aminophenyl)methane; BAPE-*bis*(4-aminophenyl)ether

[c] See text for structure

All polyamides prepared in this study were solids soluble in concentrated sulfuric acid (Table II). The polyamides from aliphatic diamines were also soluble in trifluoroacetic acid, and the polyamides from aromatic diamines also dissolved in dimethylacetamide containing 4% LiCl.

Analysis by differential scanning calorimetry showed that the polyamides of fumaric acid and aromatic diamines did not exhibit either a transition or melting point in the temperature range between -100 and +300°C (Table II). The melting temperature for the polyamides from the aliphatic diamines decreased with the aliphatic chain length and with substitution on the N atom. All of these polymers decomposed at temperatures slightly above their melting points.

TABLE II

Solubility and Thermal Characteristics
of Fumaric Acid Polyamides

Polymer[a]	Solubility[b]			T_m °C[c]	TGA Analysis	
	H_2SO_4	TFA	DMAC		Onset of decomp., °C	Mass Loss at 500°C
1	+	+	-	d	240	60
2	+	+		330	300	63
3	+	+	-	-	200	74
4	+	+	-	317	-	-
5	+	+	-	305	-	-
6	+	+	-	144	300	96
7	+	+	-	d	200	91
8	+	+	-	d	300	57
9	+	+	-	d	200	77
10	+	-	+	d	350	40
11	+	-	+	d	300	52
12	+	-	+	d	300	48
13	+	-	+	d	300	46
14	+	-	+	d	300	51

[a] See Table I for sample identification

[b] TFA - trifluoroacetic acid; DMAC - dimethylacetamide with 4% LiCl

[c] d-decomposition occurred at or before 300°C without a transition observed on DSC analysis

Thermal gravimetric analysis was used to study the thermal stability of the fumaric acid polyamides (Table II). It was found that all polymers which were obtained from the reaction of BDPF as the active diester monomer began to decompose at about 300°C (Table II) while the polyamides prepared using the FBBT monomer began to decompose at about 200°C. As another measure of thermal stability, isothermal weight loss at 500°C was determined. The most stable polymers were the fumaric acid polyamides from aromatic diamines and piperazine, and the least stable were those from the substituted aliphatic diamines.

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