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Functional polyamides

1. New polymeric azo initiators from formaldehyde and azo-dinitriles

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SUMMARY

Polymerization of azo initiators having dinitrile functions such as 2,2´-azobis(isobutyronitrile) (AIBN) with formaldehyde in the presence of sulfuric acid were carried out in order to permit the synthesis of polyamides containing thermolabile azo groups.The obtained polyamides have appropriate initiating functionality for subsequent free radical polymerization.

INTRODUCTION

Polymeric azo initiators have been used to synthesize block and graft copolymers via a radical mechanism[1].They can be prepared by means of condensation[2-5], cationic[6-9] and anionic[10,11] polymerization reactions.An alternative method for preparing prepolymers containing thermolabile azo groups involves the partial decomposition of a multifunctional azo initiator in the presence of a monomer.Block copolymers are obtained by decomposing the remaining azo groups in the presence of a second monomer[12].

It was shown[13-15] that dinitriles react with formaldehyde at low temperature in the presence of strong acids such as sulfuric acid or formic acid to give poly(monomethylene amides) according to the following reaction.

$$\text{NC-R-CN} + \text{CH}_2\text{O} \xrightarrow{H_2SO_4} \text{-[NH-CO-R-CO-NH-CH}_2\text{]-} \qquad (1)$$

A promising pathway was opened by the application of the same reaction principle to the well known azo initiator, 2,2'-azobis (isobutyronitrile) (AIBN), possessing both central thermo- sensitive azo and dinitrile functions.

EXPERIMENTAL

Materials:

AIBN (Fluka) was recrystallized from acetone.2,2'-Azobis (cyclohexanonitrile) (V-40) was a gift from Wako Chemicals and used without further purification.Trioxane (Aldrich) was recrystallized from diethylether.Styrene (St) and methyl methacrylate (MMA) were purified according to conventional drying and distillation procedures.

Polymerization Procedures:

Polyamidation:

The polymerization of AIBN with formaldehyde was carried out as follows.Trioxane (0.15 g, 0.0017 mol) was dissolved in a given amount of 95 % sulfuric acid and 0.88 g (0.005 mol) of AIBN were added with stirring over a period of 10 minutes at 0° C.Rapid polymerization occurred immadiately after the addition of AIBN and the viscosity of the solution increased gradually during the polymerization process.After one hour the solution was poured into ten-fold excess water or acetone.The resulting polymer was filtered and dried under vacuum at room temperature.

Free Radical Polymerization:

Appropriate solutions of St or MMA in DMSO / CH_2Cl_2 (1/1; v/v) containing a given amount of the above obtained polyamides were degassed in the usual manner.After heating at 70°C in a thermostated bath for 90 minutes, the solutions were poured into methanol.The obtained polymers were then filtered, dried and weighed.

Analysis:

IR spectra were recorded on a Shimadzu IR-400 using KBr discs. G.P.C chromatograms were obtained using Knauer M 64 instrument using THF as the eluent at a flow rate of 1 ml/min..The molecular weights were calculated according to polystyrene standards.

RESULTS AND DISCUSSION

AIBN was permitted to react with trioxane in sulfuric acid according to reaction 1 (R=$-CH_3)_2C-N=N-C(CH_3)_2-$).The results of the polymerization for various molar ratios of sulfuric acid are summarized in Table 1.

Table 1
Polymerization of AIBN with Trioxane in Sulfuric Acid[a]

Code	H_2SO_4/AIBN (mol /mol)	Trioxane (mol)	Yield (%)	$\eta_{sp/c}$ [b] (dl/g)
PA-1	5	0.0017	51.01	-
PA-2	10	0.0017	48.02	2.3
PA-3	15	0.0017	32.36	1.5
PA-4	20	0.0017	40.81	0.7
PA-5	25	0.0017	38.52	0.09

[a] Temperature 0°C,reaction time 60 min.
[b] Measured at 25°C in DMSO / CH_2Cl_2 (1/1, v/v)

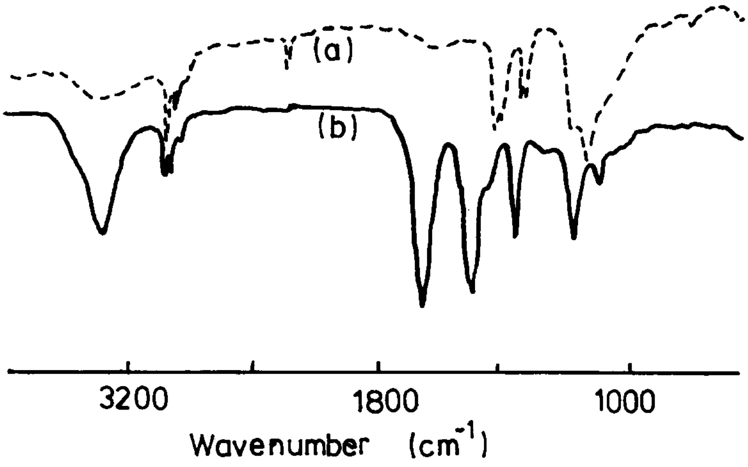

Figure 1: Infrared spectra of (a) AIBN (---) and (b) polyamid obtained from AIBN (—)

As can be seen, the yield of polymerization and the molecular weight of the polymers increased by increasing concentration of AIBN in sulfuric acid.The resultant polyamides were soluble in sulfuric acid, formic acid, m-cresol and a mixture of DMSO and CH_2Cl_2, and partially soluble in acetone.The infrared spectrum of a typical macroazo-intiator is shown in Figure 1b.The polyamid structure was easily characterized by the strong NH and C=O stretching bands appearing at 3300 and 1650 cm^{-1}, respectively, and by the disappearance of nitrile absorbtion at 2200 cm^{-1}.

A cycloaliphatic azo initiator, V-40, was also used in the polyamidation experiments in a manner similar to AIBN.The infrared spectra of the initial low molar mass azo initiator and the polyamide, which showed similar bands to that of the polyamide obtained from AIBN, are shown in Figure 2.

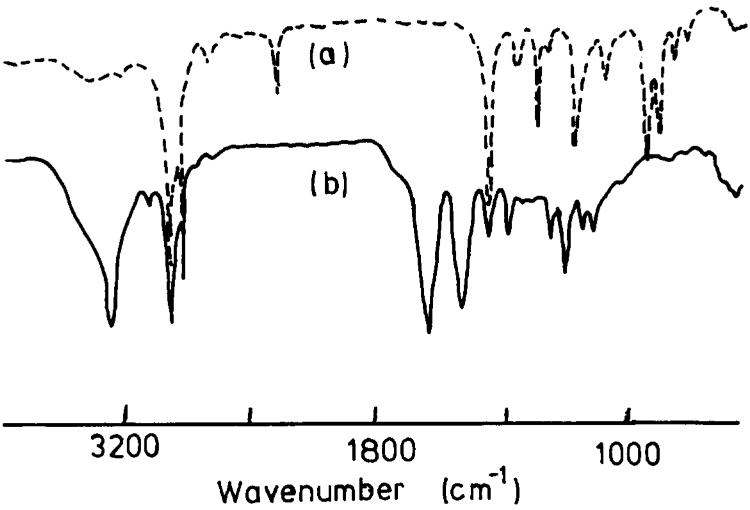

Figure 2: Infrared spectra of (a) V-40 (---) and (b) polyamid obtained from V-40 (—)

St and MMA were used as representative monomers to test the efficiency of the polyamid for initiating free radical polymerization.The results are collected in Table 2.

For a molecular design, it is essential to synthesize a polyamide having the desired number of thermolabile azo groups in the main chain since the azo concentration regulates the segment length of the polyamide incorporated to the vinyl block.Further studies along these lines are in progress in which aliphatic dinitriles having no azo functions together with AIBN are being used.

Table 2

Polymerization[a] of St and MMA initiated by PA-2 at 70°C

Monomer (mol/l)	[PA-2] (g/l)	Conversion (%)	$\eta_{sp/c}$[b] dl/g	$\bar{M}_n \times 10^{-4}$ (g/mol)	$\bar{M}_n/\bar{M}_w$
St(4.5)	10	7.39	0.41	4,9	2.20
St(6.8)	10	4.34	0.53	-	-
St((6.8)	5	4.31	0.68	8.1	2.25
MMA(4.5)	10	37.07	0.53	-	-
MMA(6.7)	10	30.75	0.59	-	-
MMA(6.7)	5	27.47	0.74	-	-

[a] Polymerization time 90 min.

[b] Measured at 30 °C in toluene

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