

Rigid rod polymer from 2,5-diaminoterephthalamide (DATA) and terephthalic acid; facile synthesis of DATA Poly[1,4-phenylene-pyrimido(4,5-*g*)quinazoline-4,9-dione-2,7-ylene]

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(Received 19 October 1992; revised 26 February 1993)

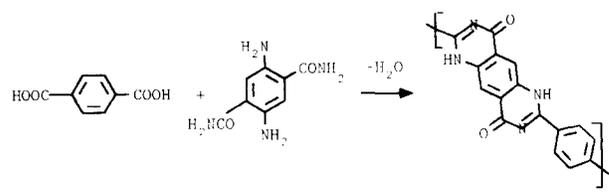
A simple, high yield synthesis of 2,5-diaminoterephthalamide (DATA) from 2,5-dicarbomethoxy-1,4-cyclohexanedione (succinoyl succinate) in two steps was developed: amination with ammonium acetate followed by aromatization in the same pot; the enamino ester was ammonolysed in a second step with excess NH_3 . Direct polycondensation plus cyclization of DATA with terephthalic acid in strong acid gave much better results than polycondensation of DATA with terephthaloyl dichloride in *N*-methyl pyrrolidone/ CaCl_2 followed by cyclization in dehydrating strong acid. The polymer showed a disappointingly low solubility. The high viscosity and unfavourable viscoelastic behaviour at low concentration hindered satisfactory spinning and only disappointing fibres were collected. Higher concentrations — that should have furnished nematic solutions with low viscosity and favourable viscoelasticity — could not be reached in the solvent systems studied.

(Keywords: DATA; terephthalic acid; 2,5-dicarbomethoxy-1,4-cyclohexanedione; terephthaloyl chloride; methane sulfonic acid; oleum; pyrimidone; oxazinone)

INTRODUCTION

Impressive fibres have been made from polybenzobisazole rigid rod polymers in recent years^{1,2}. We have attempted to further improve upon this concept by increasing intermolecular cohesion — which in the case of the benzobisazoles depends on van der Waals forces alone. Thus, we studied the 2,5-diaminoterephthalic acid series. The literature provides a synthesis from 2,5-dicarbomethoxy-1,4-cyclohexanedione (succinoyl succinate, SCSC) by melting it with a large excess of ammonium acetate (NH_4OAc), followed by aromatization with bromine in concentrated H_2SO_4 , to make 2,5-diaminoterephthalate esters³. The adduct of SCSC with benzylamine (and polymeric analogues) and its aromatization with air in hot acetic acid or with bromine in hot CCl_4 has been described⁴. Oligomeric condensates of SCSC with *m*-phenylene diamine and oxydianiline were made, and their aromatization was attempted⁵; higher molecular weights were reached with analogues using aliphatic diamines^{6,7}. (For analogous conversions of β -diketones to enaminones, see reference 8.) Ammonolysis of the diaminoterephthalate esters is impossible according to the literature³, the only rewarding reaction of the refractory ester being hydrolysis to diaminoterephthalic acid. The literature mentions 2,5-diaminoterephthalamide (DATA) as part of a study of thermally stable polymers⁹. This precedent involved a multistep synthesis of DATA

from diaminoterephthalic acid via tosylation of the amino groups, conversion to the acid chloride, and finally ammonolysis, polymerization with terephthaloyl dichloride (TDC) in *N*-methyl pyrrolidone (NMP)/LiCl and claimed a reduced viscosity (η_{red}) of 1.02 (0.5%, hexamethyl phosphoric triamide). Thermolytic cyclization of the polymer produced not only water but also some NH_3 , suggesting the formation of some oxazinone units along with the desired pyrimidone rings⁹. We envisaged cyclization in solution, with perhaps better selectivity at much lower temperature ($<150^\circ\text{C}$ instead of $>340^\circ\text{C}$). Direct polymerization and cyclization in the spinning solvent would be an even better achievement (Scheme 1).



Scheme 1

The solubility of the cyclized polymer was a point of concern from the outset, pyrimidones having more acidic than basic character, and in view of the high crystallization energy expected for such a rigid rod polymer.

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EXPERIMENTAL

Commercially available starting materials were used as received. The optimized procedures are given in detail below.

Dimethyl 2,5-diaminoterephthalate (DMDAT). The methyl ester of SCSC, (114 g, 0.5 mol), NH_4OAc (96 g, 1.25 mol) and n-butanol (1200 ml) were stirred and heated. At 80°C the colour of the mixture changed to orange (clear solution). After 20 min the mixture was boiling; from 105°C the enamine formed began to crystallize. The mixture was kept at the boil for 1 h and then sulfur (17.6 g, 0.55 at) was added. After 1 h of refluxing the mixture was clear and dark red in colour. A further 2.5 h of refluxing completed the reaction. With very slow stirring the mixture was cooled to room temperature and filtered with suction. The filter cake was sucked dry and transferred to a beaker and stirred with CCl_4 for 90 min. Filtering with suction and drying for 16 h at 100 Pa gave a 80.23 g (71.6%) yield of red DMDAT; m.p. 181–187°C. I.r. (KBr): 3460, 3360, 1685, 1580, 1500, 1435, 1285, 1220, 1105, 900 and 790 cm^{-1} . (The dihydro analogue has i.r. peaks at 3430, 3320, 1670, 1610, 1565, 1435, 1285, 1230, 1095, 1015, 780 and 770 cm^{-1}). ^1H n.m.r. (DMSO): 3.81 (Me ester), 5.80 ($-\text{NH}_2$), 7.28 (aromatic H) ppm singlets, 3:2:1 integrals. Using the mother liquor from the first filtration rather than fresh n-butanol increased the yield to 75.2%.

2,5-Diaminoterephthalamide (DATA). DMDAT (112 g, 0.5 mol), ethylene glycol (EG, 200 ml) and (liquid) NH_3 (190 g, 11 mol) were stirred in a 2 l autoclave at 140°C for 4 h (at 6 MPa). After cooling and venting the mixture was filtered with suction and washed with ethanol. Recrystallization from DMF gave a 72.5 g (75%) yield of yellow DATA; m.p. 311–318°C. I.r. (KBr): 3390, 3310, 3180, 1690, 1570, 1395, 1320, 1230, 1160, 1080, 880, 860; multiplet 800, 765, 725, 700, 625, 575, 500, 460; 415 and 360 cm^{-1} . ^1H n.m.r. (DMSO): singlets at 5.36 (amine), 6.85 (aromatic H), 7.16 and 7.70 (amide) ppm.

Polymerization (cf. Table 1). A mixture of DATA (1.94 g, 10 mmol), terephthalic acid (TPA, 1.66 g, 10 mmol) and methanesulfonic acid (MSA, 97.5 g) were stirred in a reaction flask under nitrogen. After 15 min 65% oleum (17.8 g, 145 mmol of SO_3) was added. The mixture was heated with stirring at 100°C. This resulted in a clear

solution after 2 h. Polycondensation with cyclization was completed by further stirring at 100°C for 48 h. The solution was then ready for use in spinning experiments or for film making with a doctor blade, with coagulation in water.

I.r. (film): 3620, broad band 3400–2200 peaking at 3091, 1772, 1685, 1540, 1418; broad band at 1300, 1117, 1015, 919, 870, 790, 714 and 525 cm^{-1} . ^{13}C CP/MAS n.m.r.: 117.6 (DATA $\text{C}^{1,4}$), 127.9 (strong, DATA $\text{C}^{3,6}$ and terephthalic $\text{C}^{2,3,5,6}$), 137.7 and 134.3 (DATA $\text{C}^{2,5}$ and terephthalic $\text{C}^{1,4}$), 162.2 (terephthalic carboxyl C incorporated in heterocyclic ring) and 171.5 (DATA carbonyl) ppm from TMS.

Polycondensations in other media were conducted by first preparing the solution in MSA and then adding pure SO_3 rather than oleum (Table 2) or just by dissolving the monomers in 20% oleum or 84% polyphosphoric acid and then heating (Table 3). The NMP/ CaCl_2 runs were performed by first dissolving DATA (a slow process) and then adding the terephthaloyldichloride (TDC) in one portion with stirring at room temperature, and optionally heating (Table 4).

RESULTS AND DISCUSSION

In early work it proved difficult to aromatize **1** to **2** by simply heating with a noble metal catalyst (Scheme 2).

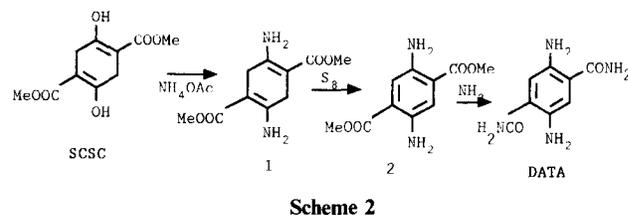


Table 2 Polycondensations of DATA with TPA in MSA and SO_3 at 100°C^a

MSA (g)	SO_3 (g)	Reaction time (h)	η_{rel} (0.5% MSA)	Comments
63.6	6.4	21	Insoluble	Gel
64.1	7.9	18	5.16	High viscosity fibre forming
62.4	9.6	28	5.69	High viscosity fibre forming

^a Polymer concentration 4%. Experiments duplicating those presented but with reaction temperatures of 120 or 150°C gave gelled reaction masses in most cases

Table 1 Polycondensations of DATA with TPA in MSA with 65% oleum

Oleum (g)	MSA (g)	Polymer concentration (%)	η_{rel} (0.5% MSA)	Reaction mass character ^a
18.2	54.7	4	1.90	High viscosity (0.10% S)
12.7	59.2	4	1.47	
29.5	44.4	4	–	Paste
12.6	59.2	4	–	Gel
7.2	64.8	4	Insoluble	Gel
12.7	61.3	4	2.91	After 19 h at 100°C
			5.92	Plus 22 h at 120°C
12.7	102.5	2.5	3.59	Some gel particles?
17.8	97.5	2.5	3.70	48 h at 100°C, no gel

^a Reaction temperature 150°C

Using air under Wacker-like conditions seemed possible in principle but the danger of over-oxidation was demonstrated immediately. Aromatization with sulfur, another classical approach, proved easy — at first in a fast reaction at $\sim 175^\circ\text{C}$ in NMP, later in a slower reaction in boiling *n*-butanol. The attraction of *n*-butanol lay in the fact that we found the first stage amination to proceed very well with a small excess of NH_4OAc in *n*-butanol (other media tried, with less success, were *m*-xylene, EG and butanediol).

Ammonolysis of the ester being difficult was verified, but the ester was not so strongly deactivated that alcohol was not rapidly eliminated from it in a situation where that process was unwelcome — in polymerization of the ethyl ester with TDC in NMP/ CaCl_2 early cyclization to oxazinone liberates ethanol which quenches some of the TDC — thus preventing high molecular weights being reached. An exploratory experiment with NaNH_2 in NH_3 at high temperature showed that the ester can be directly converted to the amide under forcing conditions. Poor and variable results were obtained with supercritical NH_3 . Using NMP as a solvent actually stopped the reaction. Reasoning that a strongly hydrogen bonding and high-boiling solvent would help increase the NH_3 concentration in the liquid phase at temperatures above the critical temperature for NH_3 , we tried EG as the solvent for the ammonolysis. This approach met with immediate success. The reaction temperature could now even be decreased — the high dielectric constant of EG probably assisting in the reaction, compared with NH_3 alone. The product was filtered off in a fairly pure state from the reaction mixture in EG and was recrystallized from DMF. Use of a larger amount of EG in the ammonolysis may eliminate the need for recrystallization.

A programme was carried out aimed at integrating all three reaction steps into a single-pot process. EG, 1,4-butanediol and pinacol were screened. EG gave poor results in the ammonolysis/aromatization step; butanediol performed well in that step but performed poorly in the ammonolysis. Pinacol was studied as a non-nucleophilic 1,2-diol with a view to minimizing ester byproduct in the ammonolysis arising from reaction of

starting material with (excess) solvent in the ammonolysis equilibrium. Low conversion was noted, however. So far, we have eliminated the excess sulfur from the aromatization step (which is needed for a high-yield reaction) from the first-step crystallization by stirring with CCl_4 . Whether this operation is necessary to avoid the presence of sulfur in the final product is uncertain; an alternative might be a similar treatment of the final product. An attempt to use NH_3 for the first step and maybe integrate the first and third transformations, and aromatize as the last step gave a complex mixture that we attribute to ester condensation pathways.

Our polymerizations in organic solvent (NMP/CaCl_2)¹⁰ provided polymers with η_{rel} values up to 0.9 (0.5%, 96% H_2SO_4). Direct polymerization of DATA with TPA in oleum (the free SO_3 present to bind water formed in the condensation reaction) appeared to proceed successfully in principle but the polymers precipitated from the reaction medium, and were insufficiently soluble in 96 or 100% H_2SO_4 to even allow solution viscosity measurement. Such data could be obtained in MSA. Solvents tested for our polymer system included NMP/ CaCl_2 (best), NMP (reasonable), dimethylacetamide (DMAc)/LiCl, DMAc and NMP/ ZnCl_2 (poor results for prepolymer dissolution). Swelling paralleled the dissolution trends. For the cyclized polymer: MSA (best), H_2SO_4 (reasonable), polyphosphoric acid (poor). We decided to evaluate MSA as the polymerization solvent, in combination with oleum or pure SO_3 to provide the

Table 4 Polymerizations of DATA with TDC in NMP (first experiment) or a NMP/ CaCl_2 mixture (PpPTA^a polymerization solvent system, cf. ref. 1). All products were soluble in H_2SO_4

Polymer concentration (%)	Reaction time (h)	Reaction temperature ($^\circ\text{C}$)	η_{rel} (0.5% in 96% H_2SO_4)
4	60	20	1.07
2	60	20	1.28
10	60	20	1.08
10	7	80	1.09
1	40	20	1.36

^a PpPTA, poly(*p*-phenylene terephthalamide)

Table 3 Polymerizations of DATA with TPA in 20% oleum or polyphosphoric acid (84% P_2O_5)

Polymer concentration (%)	Reaction time (h)	Reaction temperature ($^\circ\text{C}$)	η_{rel} (0.5% MSA)	Comments (Elemental analysis)
Oleum				
5	2.5	150	1.67	Solidified reaction mass XRF 0.20% S
5	4	120	1.42	Solidified (0.18% S)
10	2.5	120	—	Solidified
5	27	100	1.34	Solidified
4 ^a	8	120	1.61	Paste
Polyphosphoric acid				
5	2	150	—	Paste (1.97% P)
5	16	120	—	Gel (1.74% P)
5	40	100	1.34 ^b (0.5%, H_2SO_4)	(2.55% P)
10	24	100	—	Solidified (1.90% P)

^a Polymerization with TDC in NMP/ CaCl_2

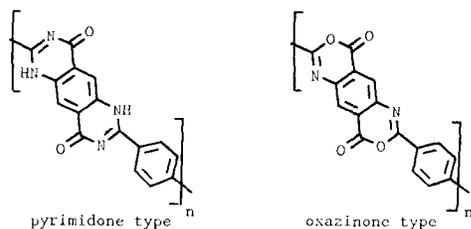
^b None of the products were sufficiently soluble in H_2SO_4 (96%) to allow η_{rel} measurement except for one polyphosphoric acid run

driving force for the polycondensation. This approach proved appropriate for the preparation of high molecular weight polymers (η_{red} values >9 being attained), but the solubility of the products in MSA proved limited ($<5\%$). Even 5% could not be reached if care was not taken to limit the amount of the poor solvent (H_2SO_4) in the solvent system to a minimum, i.e. using very strong oleum or pure SO_3 in a modest excess, to keep the polymerization mass from turning into a gel- or paste-like mixture. Polymerization temperatures over $100^\circ C$ often led to crosslinked polymers. The low polymer concentrations attainable prevented the fabrication of attractive yarns, and no liquid crystallinity of these dilute solutions was encountered. Wet-spinning produced yarns with tenacity <30 cN tex $^{-1}$, modulus of elasticity <13 N tex $^{-1}$ and elongation at break = 10–17%.

Alternatives that were briefly explored in polymerization were: isochinomeronic acid instead of TPA to promote polymer solubility. This diacid failed to enter into direct polycondensation, which we rationalize by the high energy of pyridinium acylium dications — the pyridine nitrogen will be protonated all of the time in MSA/oleum. The diacid chloride was prepared and its polymerization with DATA attempted, but low molecular weights were again obtained (in NMP/ $CaCl_2$ the pyridine unit in isochinomeronic acid will not contribute much enhanced solubility compared with TPA). Polyphosphoric acid was studied as the medium for direct polymerization; insoluble products containing sizable amounts of phosphorus (by X-ray fluorescence) were obtained. By contrast, the polymers prepared in H_2SO_4 or MSA/oleum or MSA/ SO_3 contained only slight traces of sulfur which we attribute to residual solvent remaining after practical rather than perfect washing.

Terephthalonitrile instead of TPA gave low molecular weight polymers in MSA with a small addition of oleum, and with larger amounts of oleum the polymer formed again became insufficiently soluble. The nitrile was intended to eliminate (almost) all need for H_2SO_4 from the solvent system, since NH_3 rather than water would have to be eliminated in the polymerization plus cyclization: SO_3 would be needed only as a safeguard against traces of water in the MSA. Methanesulfonyl chloride was evaluated as the dehydrating agent rather than SO_3 ; it led to gel formation.

Analysis of the polymers was attempted by solid state ^{13}C CP/MAS n.m.r. experiments with both PENMRFB and PENPC.P programs¹¹. This study suggests that cyclization has occurred as desired, i.e. forming pyrimidone units. In particular, failure of the carbonyl-C related resonances to shift to substantially lower field in the cyclized polymer (169.3 and 164.1) relative to the amide groups in the non-cyclized (pre)polymer (171.8 primary, 161.6 secondary amide) supports this conclusion. FTi.r. work employing a freshly made film suggests the presence of non-negligible oxazinone functionality (1772 cm^{-1}) in addition to pyrimidone (1690 cm^{-1}), but only pyrimidone in fibre



and in cyclized model compounds (see below); ageing the film for >4 weeks in ambient air somehow destroys the oxazinone signal (by hydrolysis?)¹².

Elementary analysis gave incomplete assays (totalling $<<100\%$), in line with the very difficult destruction of these polymers. These data suggested oxazinone type cyclization plus bound water, with far higher oxygen than nitrogen figures. Model compounds were prepared from DATA and benzoyl chloride (prepolymer model), DATA and benzoic acid in MSA/oleum (polymer model) and the prepolymer model was subjected to MSA/oleum cyclization in a second step. The model compounds could be analysed by solution and by solid state n.m.r.¹¹ as well as by Fourier transform infra-red (FTi.r.) spectroscopy¹². The prepolymer model was identified unambiguously; the cyclized model products were identified as cyclized to pyrimidone derivatives (FTi.r.; 1H , ^{13}C and ^{15}N n.m.r.), but the benzoic acid rings had been sulfonated (benzoyl rings being much more susceptible to sulfonation than terephthaloyl rings). Since this sulfonation might influence the chemoselectivity in the cyclization, the model compound work did not fully resolve the question. The fact that excess SO_3 was required during the polymerization relative to 2 moles of water per carboxylic group in the TPA rather than relative to 1 mole, suggests the cyclization to have occurred in the desired (pyrimidone type) sense — elimination of NH_3 to generate the oxazinone type ring would not require SO_3 but only acid.

CONCLUSIONS

A simple and economical process was arrived at to synthesize DATA from SCSC which is available as a fine chemical (dyestuff precursor) at a moderate price, in line with its easy availability from low cost succinic ester. DATA may be directly polycondensed with TPA in MSA and SO_3 or oleum to make high molecular weight polymer, which due to its limited solubility cannot be processed via a liquid crystalline solution. Cyclization during the polymerization proved not to be a clean process furnishing pyrimidone rings only, but produces oxazinone type rings as well, which seem to disappear with ageing of fibre or film fabricated from the polymerization solutions.

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