Polymer Bulletin 25, 17–24 (1991)

Polymer Bulletin

Polymers from Reissert compounds

7 (1) Novel thermoplastic polyamine derivatives from acyclic Reissert compounds

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Summary

A series of new polymers have been synthesized by condensation of the dianions of acyclic bis(Reissert compounds) (**A-A** dinucleophile) with dihaloalkanes (**B-B** dielectrophile). These thermoplastic polyamides (**10**) are soluble in a wide range of solvents including THF, $CHCl_3$, DMF, NMP, etc. Intrinsic viscosities vary between 0.07 and 0.48dL/g. The T_g's vary from 72°C to 116°C, depending upon the spacer derived from the electrophile. These polymers are stable up to 225°C (*in air*) and exhibit a 10% weight loss (*in air*) above 300°C.

Introduction

A functionalized derivative of isoquinoline, 1-cyano-2-benzoyl-1,2-dihydroisoquinoline **1** (commonly known as an isoquinoline Reissert compound), was first synthesized by Reissert in 1905 (2). Over the last eight decades, a variety of Reissert compounds have been made from a wide spectrum of aromatic heterocycles and acid chlorides (aliphatic and aromatic). This information and the reactions of Reissert compounds have been covered in depth in reviews (3). The Reissert moiety consists of an α-amido nitrile which renders the proton on the α-carbon acidic. Deprotonation by various bases such as PhLi, NaH, NaOH or LDA results in the conjugate base which either undergoes a rearrangement in the absence of an electrophile or substitution in the presence of an electrophile. In the case of the anion derived from **1**, 1-acylisoquinolines (**2**) result from rearrangement (3). A few substitutions, particularly the alkylations, involving the nucleophilic attack of the Reissert anion, result in quantitative yields of the substituted product. For example alkylations of the anion of **1** produce derivatives **3** in excellent yields (3). These and other reactions have been widely used in classical organic synthesis (3).

Our goal is to extend this methodology to polymerization involving novel **A-A** monomers of the bis(Reissert compound) category

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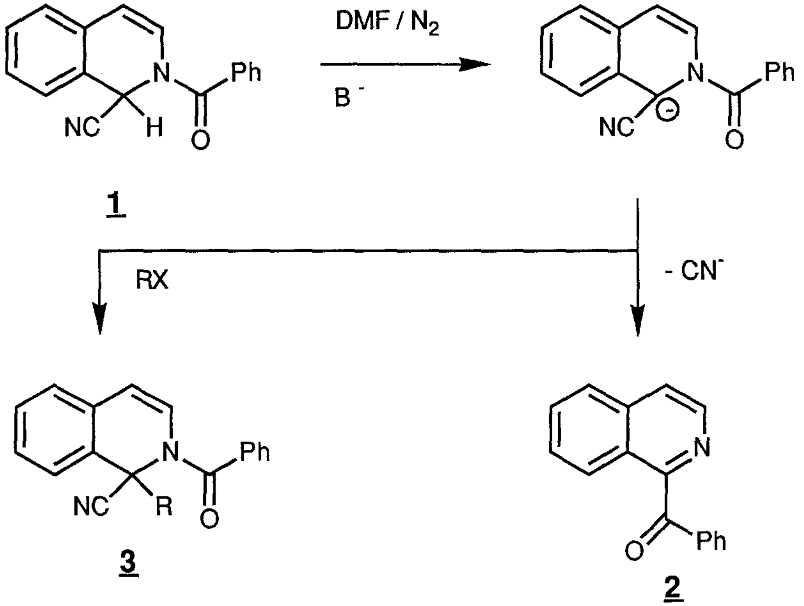
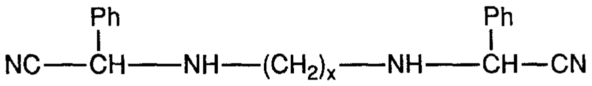
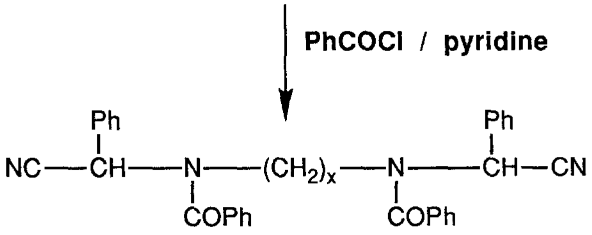
*To whom offprint requests should be sent and suitable dihalo electrophilic **B - B** monomers by the polycondensation route to yield novel polymers. We now report the successful application of this methodology, resulting in the production of novel polymers.





$$NC-\underset{}{\overset{Ph}{CH}}-NH-(CH_2)_x-NH-\overset{Ph}{CH}-CN$$

4, x = 2 ; **5**, x = 4 ; **6**, x = 6



$$NC-\overset{Ph}{CH}-\underset{COPh}{N}-(CH_2)_x-\underset{COPh}{N}-\overset{Ph}{CH}-CN$$

7, x = 2 ; **8**, x = 4 ; **9**, x = 6

Results and Discussion

A. Monomer Synthesis

Bis(aminonitriles) **4**-**6** have been quantitatively synthesized from diamines and benzaldehyde in the presence of a cyanide ion source by a multi-step one-pot aqueous method (Table 1). This is a mild, cheap, efficient and convenient method of aminonitrile synthesis. By simple acylation with benzoyl chloride, we quantitatively converted these bis(aminonitriles) to bis(Reissert compounds) **7**-**9** which represent a new class of reactive **A-A** monomers (Table 1).

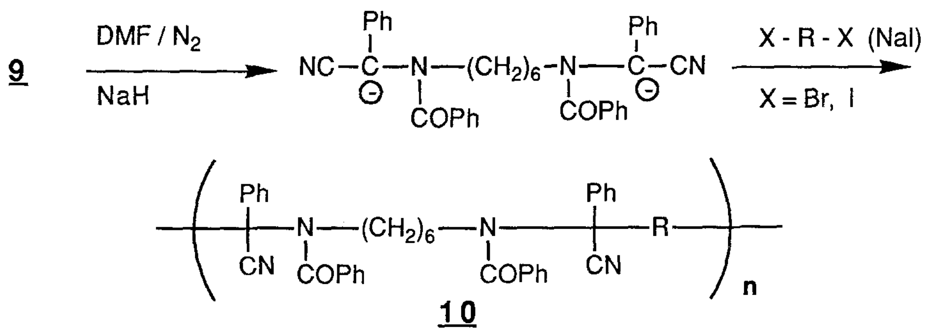
Table 1

Bis(aminonitriles) and Corresponding Acyclic Bis(Reissert compounds)

Compound	yield (%)	m p [^oC, corrected]
4	100	118 - 120 [lit. (4) 118-123]
5	100	89 - 90.5 [lit. (5) 88]
6	100	oil [lit. (5) 68]
7	100	225 - 227*
8	100	202.5 - 203.5*
9	100	169 - 170.5*

* These new compounds gave satisfactory elemental (C,H,N) analyses. Spectroscopic data (PMR, FTIR and C-13 NMR) lend ample proof of structure.

Scheme 1



10a, R = $(CH_2)_{10}$; **10b**, R = $(CH_2)_4$; **10c**, R = m-xylyl

B. Polymer Synthesis and Characterization

Condensation of these acyclic bis(Reissert compounds) **7**-**9** via their dianions with suitable dihalo aliphatics gave novel polymers with flexible spacers. The synthetic route is outlined in Scheme 1. An advantage of the acyclic systems of this type is that they do not rearrange (1b) via their anions due to the absence of the driving force of rearomatization that is involved in the conversion of **1** to **2**. In some bis(isoquinoline) Reissert compounds a rearrangement analogous to conversion of **1** to **2** is a side reaction which decreases molecular weight and increases molecular weight distribution (6).

When diiododecane (X = I, no NaI) was used with the conjugate base of **9** (37% solids initially), a gel **10a** was obtained; no overhead stirrer was employed and no salt (alkali metal halide) was used to help solubilize the polyamide. The gel was dissolved in DMF with the application of heat and precipitated in ice-water. An absolute GPC determination of molecular weights gave M_n = 14.5K and M_w = 162K. The high polydispersity is attributed to the presence of low molecular mass species trapped when gelation occured. When the concentration was halved (18% solids initially), the solution still gelled, indicating the effect of secondary interactions causing the gelation. This gelation is thermo-reversible as opposed to any crosslinking type process.

Next, NaI was added to the dibromodecane in order to generate the diiododecane in situ. This avoided the handling of the air-sensitive diiododecane. In the presence of NaI no gelling of **10a** was observed, presumably due to increased ionic strength. The resulting polymer showed a viscosity of 0.35dL/g. The same procedure using dibromobutane resulted in a polymer with a viscosity of 0.07dL/g.

Polyamides **10a**-**10c** were pale yellow or pale brown, thermally stable up to 225°C (in air) and showed a 10% weight loss above 300°C (specifically between 300 and 315°C). The intrinsic viscosities (NMP, 25°C) were between 0.07 and 0.48dL/g. Glass transition temperatures were found to be 72°C to 116°C. The decamethylene spacer being the most flexible gave the lowest T_g of 72°C. With the incorporation of the m-xylylene moiety, the T_g rose to 116°C, while the T_g was 84°C in the case of the tetramethylene spacer. No evidence of crystallinity was obtained from the DSC (2nd heat). Table 2 summarizes the results.

Table 2

Thermoplastic Polyamides from Acyclic Bis(Reissert compounds)

Polymer	Viscosity[a]	TPWL(°C)[b]	T_g(°C)[c]
10a[d,e]	0.48dL/g	305	72
10a[f]	0.15dL/g	305	72
10a[g]	0.35dL/g	305	71
10b[g]	0.07dL/g	307	84
10c[h]	0.09dL/g	300	108
10c[g]	0.08dL/g	312	116

a) intrinsic viscosities in NMP at 25°C. b) ten percent weight loss in air. c) at a heating rate of 10°C/min. d) without NaI, 37% solids initially, gel obtained and worked up upon dissolution. e) Absolute M_n = 14K, M_w = 162K. f) without NaI, 18.5% solids initially, gel obtained. g) with NaI. h) without NaI, M_n = 8.8K, M_w = 33K.

The polymer **10a** could be viewed as having a CRU of decamethylene and hexamethylene separated by an α-amido nitrile moiety. While the T_g of Nylon-6,12 is 46°C (7), the T_g of **10a** is 72°C. This 36° rise in the T_g for **10a** is attributed to the bulkiness of the phenyl groups and the secondary interactions of the polar nitrile group, despite the absence of H-bonding due to the primary amide linkages characteristic of the Nylon-6,12. Polyamides **10** are derivatized linear polyamines. This is unique since there are very few linear aliphatic polyamines known due to the problems of branching. Exceptions are the polyethyleneamines derived by hydrolysis of polyoxazolines, made by the "no catalyst polymerization via zwitterionic intermediates"; these, however, usually have low molecular masses (8).

Proton NMR spectra of these polymers showed the usual broadness of the peaks associated with polymeric materials due to the presence of tacticity. The Reissert compound derived polymers have two stereogenic centers per CRU, each of which is capable of existing in the R or S configuration. All showed peaks in the appropriate aromatic and aliphatic regions, the integration ratio of which matched exactly with the theoretical expectations. FTIR spectra lend proof of structure and show broad absorptions of the amide carbonyl and a very, very weak nitrile peak.

Conclusion

Novel thermoplastic polyamides have been prepared. The ease of preparation, high yields and economical aspects of the reactants are noteworthy. By variation of the aldehyde and diamine components of the bis(aminonitriles), the acyl groups of the bis(Reissert compounds) and the spacer of the electrophilic component (R of **10**), the physical properties can be widely varied. We are now exploring these structural variables (9).

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also gratefully acknowledge financial support from the Center for Adhesion and Sealant Science (CASS), Va. Tech. for an assistantship (to AP), Prof J. E. McGrath and Prof. T. C. Ward for helpful discussions and absolute GPC analyses.

Experimental

Monomers were either triply recrystallized or vacuum distilled prior to use. NaI (Fisher Biotech grade, 99+%) was dried at 100°C in vacuo. DMF used for polymerization was purchased from Aldrich (Sure Seal). Melting points were determined on a Haake Buchler melting point apparatus and are corrected. Thermogravimetric analyses were carried out on a Perkin Elmer 7700 TAS (thermal analyses system) in air atmosphere. Glass transitions were determined at a 10°C/min heating rate by a single cell instrument of the Perkin Elmer 7700 Thermal Analyses System. Proton NMR spectra were recorded on a Bruker 270 MHz instrument interfaced to an Aspect 2000 and a Hewlett Packard 7550A graphics plotter. Tetramethylsilane was used as the internal standard. FTIR spectra were recorded on a Nicolet MX-1. Absolute GPC analyses were run using a Viscotek model #100 differential viscosity detector and a Waters 150C equipped with a RI detector operating at 60°C with DMF (0.5% LiCl) eluant.

Synthesis of N,N'-Bis(α-cyanobenzyl)-1,4-butanediamine (5) :

To a solution of 19.8 g (192 mmol) of $NaHSO_3$ in 300 mL of water were added 19.6 mL (192 mmol) of benzaldehyde and the mixture stirred vigorously for two h to give a homogeneous colorless solution of the bisulfite addition product. 8.4 g (96 mmol) of 1,4-butanediamine were then added in one aliquot and the stirring continued for two h to give a colorless solution to which were added 9.6 g (192 mmol) of NaCN in one aliquot. The stirring was then continued for 8 h and the sticky solid was dissolved in CH_2Cl_2 and the organic layer was washed with water (6x, 100 mL each), dried over Na_2SO_4 and concentrated to give a pale oil that crystallized upon standing, 30.4g (100%). Recrystallization from EtOAc gave shiny white needles, mp 89-90.5°C [lit (5) 88°C]. Proton NMR : 7.6-7.4δ (m, 5H), 4.8δ (s, 1H), 2.9-2.7δ (2 br. overlapped triplets, 2H), 1.7δ (br. s, 1H), 1.6δ (br. s, 1H). FTIR : 3342 cm^{-1} (sh., amine), 2228 cm^{-1} (str., CN), 1119 cm^{-1} (str., C-N), 743 cm^{-1} (v. str., methylene rock).

Synthesis of N,N'-Bis(α-cyanobenzyl)-N,N'-dibenzoyl-1,4-butanediamine (**8**) :

6.36 g (50 mmol) of **5** were dissolved in 100 mL of dry pyridine under N_2 and cooled to 0-5°C. To the off-white solution were then added 12.7 mL (105 mmol) of BzCl. The solution was stirred overnight and quenched by pouring in 1500 mL ice-water mixture. The white solid was filtered, washed thoroughly with water and dried, 10.5 g (100%). It was recrystallized from DMF-EtOH (8:1) to give a white solid, mp 202.5-203.5°C. Elemental analysis, found (theory), C : 77.28 (77.54), H : 5.78 (5.74), N : 10.57 (10.64). Proton NMR : 7.5δ (m, 11H), 3.2-2.9δ (2 br. overlapped triplets, 2H), 1.4, 1.0δ (2 br. overlapped triplets, 2H). FTIR : 2243 cm^{-1} (v. weak, CN), 1636 cm^{-1} (amide), 1600 cm^{-1} (aromatic C=C).

Polymer syntheses :

The monomers were weighed accurately on an analytical balance to a stoichiometric equivalence and dissolved in DMF. NaI was added and then NaH [2.2 equivalents per bis(Reissert monomer)] was added. After stirring for over 3 days at ambient the mixture was quenched in ice-water. The resulting polymers were purified by dissolving in DMF-THF (1:6) and precipitation into tenfold excess H_2O-MeOH (2:1 v/v) three times and dried in vacuum 20° below T_g. A typical synthesis is given below.

Synthesis of (**10a**) :

4.0100 g (7.2304 mmol) of **9** were dissolved in 31 mL of dry DMF in a flame dried flask with the application of heat. The colorless solution was allowed to cool to ambient temperature and then 2.1704 g (7.2324 mmol) of 1,10-dibromodecane were quickly added along with 3.5 g (23 mmol) of NaI and the mixture stirred under N_2. After about 15 min, 635 mg (15 mmol) of NaH (60% suspension in oil) were quickly added and the reaction mixture was srirred for 72 h at ambient temperature. Evolution of H_2 and a deep red color (of the dianion) were immediately noticeable. An increase in viscosity was noted over the reaction time. The reaction was quenched by pouring into 12 fold excess brine-ice-MeOH (3:8:1 v/v) in a high speed blender to yield 4.98 g (100%) of pale yellow solid. Precipitation from THF-DMF (8:1 v/v) into 12 fold H_2O-MeOH (2:1 v/v) was carried out three times. The resulting pale brown polymer was dried at 50°C in a vacuum oven overnight.

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Accepted August 31, 1990 K