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Acyclic Polymeric Reissert Compounds: Chemically Reactive Polyamides. 3[1,2]

Jean-Pierre Leblanc and Harry W. Gibson*

Department of Chemistry and NSF Science and Technology Center for High Performance Polymeric Adhesives and Composites, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0212

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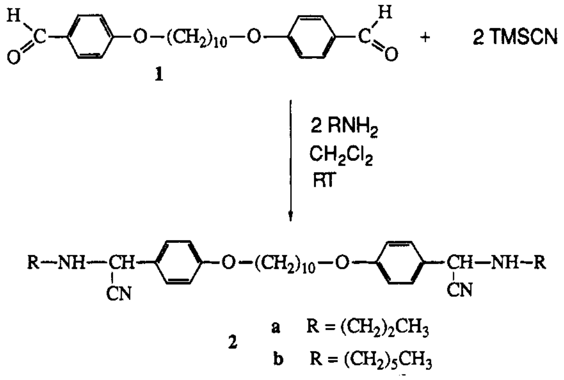
ABSTRACT: Polymeric Reissert compounds were prepared by condensation of bis(α-amino nitrile)s derived from dialdehydes containing a flexible spacer with adipoyl chloride and by acetylation of polymeric α-amino nitriles which resulted from reaction of dialdehydes with diamines. Alkylation of one of the polymeric Reissert compounds was carried out.

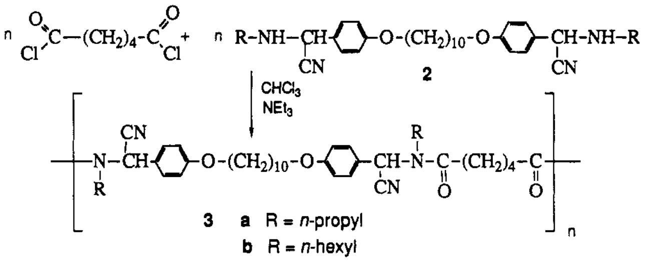
Introduction

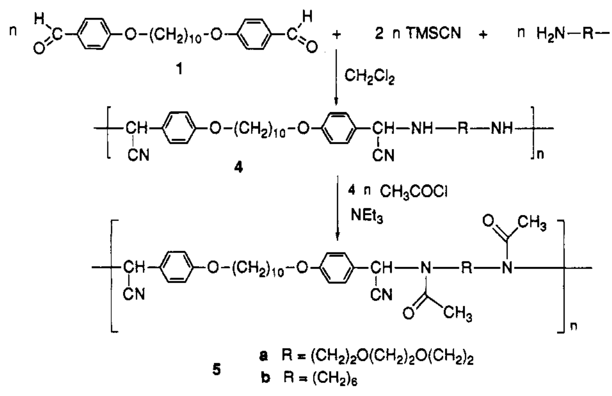
The incorporation of acyclic Reissert (α-cyano amide) moieties into polymers or copolymers allows one to extend the peculiar chemistry of these compounds[3] to polymeric substrates. A thermal cyclization of such polymers has been reported to give poly(phenyleneimidazolinone)s.[4] Our previous efforts in preparing such polymers have included the condensation of adipoyl chloride with a terephthaldehyde-based bis(α-amino nitrile)[5] and with diamine-based bis(α-amino nitrile)s.[1] Weight-average molecular weights of 20 000 were achieved when sufficient hindrance and/or spacing between the α-amino nitrile moieities of the monomer was present. We present here the condensation of bis(α-amino nitrile)s containing flexible spacers. A novel approach, based on the acylation of poly(α-amino nitrile)s, is also described as well as an alkylation experiment.

Results and Discussion

The preparation of bis(α-amino nitrile)s from the dialdehyde 1 could not be achieved using a classic Strecker procedure due to the hydrophobicity of this compound. Its conversion to bis(α-amino nitrile)s was rendered possible in an organic solvent using TMSCN (trimethylsilyl cyanide) as the organic source (Scheme I).[6] The crystalline bis(α-amino nitrile)s **2** were condensed with adipoyl chloride by addition of the diamino monomer onto adipoyl chloride as described previously (Scheme II).[1] Polymers **3a** and **3b** were obtained, with respective intrinsic viscosities 0.36 and 0.46 dL g^{-1} (CH_2Cl_2, 25 °C). As substituted polyamides incorporating flexible spacers, they are amorphous in nature (very low degree of crystallinity for **3b**), soluble in common organic solvents (dichloromethane, chloroform, THF), and film-forming.


Scheme I


Scheme II


Scheme III

Since bis(α-amino nitrile)s **2** were prepared in an organic solvent, one could envisage the condensation of dialdehydes with diamines and TMSCN to generate poly(α-amino nitrile)s. This was performed from the same dialdehyde 1 and both hexanediamine and 1,2-bis(2-aminoethoxy)ethane (Jeffamine EDR-148) (Scheme III). Attempts to isolate the secondary poly(α-amino nitrile)s **4** resulted in some extent of dehydrocyanation to give azomethine units; only by precipitation of the polymer in hexanes followed by drying at room temperature under vacuum was the extent limited to less than 5%. However, addition of an excess of acetyl chloride to the poly(α-amino nitrile) converted it into the acyclic poly(Reissert compound) **5** (Scheme III). As the poly(α-amino nitrile) became acetylated the viscosity of the polymer solution decreased. This probably resulted from the loss of intermolecular H-bonding interactions. Intrinsic viscosities of 0.32 and 0.25 dL g^{-1} were obtained for **5a** and **5b**, respectively (CH_2Cl_2, 25 °C). When hexanediamine was used as the diamine, the polymeric Reissert compound **5b** showed a low degree of crystallinity with a melting point at 75 °C.

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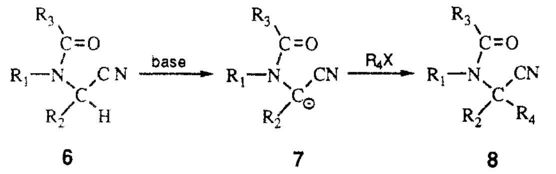
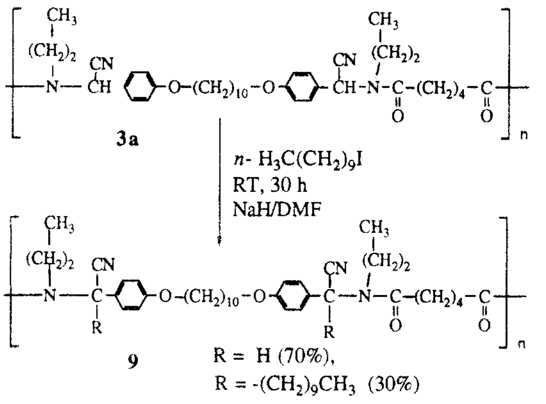
Scheme IV



Scheme V



Two routes have therefore been demonstrated for the preparation of relatively high molecular weight acyclic polymeric Reissert compounds. One interest in such polymers resides in the ability of the methine proton, the Reissert proton, to be abstracted with a base to generate the corresponding anion. The conversion of an acyclic Reissert molecule **6** to the conjugated anion **7** is shown in Scheme IV. Electrophilic attack with an alkyl halide generates the alkylated analog **8**.[7] To modify surface/bulk properties of polymeric Reissert compounds such as **3** and **5**, one may choose to employ a hydrophilic or hydrophobic alkyl halide. Hence polymer **3a** was treated with sodium hydride in dimethylformamide to give the corresponding polyanion (Scheme V). Decyl iodide was selected as the electrophile. The reaction was carried out for 30 h, and it was determined by ^{1}H NMR spectroscopy that after this length of time about 30% of the Reissert protons had been substituted with *n*-decyl grafts to give polymer **9**. The reaction appeared slower and less complete than for corresponding low molecular weight substrates because of both the hindered position of the Reissert proton (α to an aromatic ring and a substituted nitrogen atom) and the length of the alkylating agent. Some extent of cleavage may have occurred since the intrinsic viscosity of the alkylated polymeric Reissert compound turned out to be lower than that of the unsubstituted polymer (0.26 vs 0.36 dL g^{-1}). However, spectroscopic analysis did not show evidence of new groups which would have resulted from side reactions. Differences in Mark–Houwink coefficients offer another possible explanation for the variation. The substitution decreased the glass transition temperature from 36 to 24 °C.

Conclusion

Polymeric Reissert compounds have been synthesized by condensation of bis(α-amino nitrile)s containing flexible spacers with adipoyl chloride. The bis(α-amino nitrile) monomers were prepared by stoichiometric condensation of the dialdehyde **1** with amines and TMSCN. Extension to the use of diamines afforded the obtention of polymeric α-amino nitriles, which tend to dehydrocyanate upon isolation. However, their acetylation in situ to the acyclic polymeric Reissert compounds was achieved. Upon treatment of polymer **3a** with sodium hydride and *n*-decyl iodide in DMF, 30% of the Reissert units became alkylated.

Experimental Section

The preparation of the bis(α-amino nitrile)s has been published elsewhere.[6] The procedure for preparing polymers **3** has also been described.[1] Jeffamine EDR-148 was obtained from Texaco, and the other chemicals were obtained from Aldrich and Fisher.

^{1}H NMR spectra were recorded on a Bruker 270-MHz instrument using TMS as the reference and CDCl$_3$ as the solvent. FTIR spectra were recorded on a Nicolet MX-1. Elemental analyses were performed by Atlantic Microlab, Norcross, GA. DCS experiments were performed with a 10 °C/min heating rate on a Perkin-Elmer 7700 thermal analysis system. Thermogravimetric analysis was carried out at 10 °C/min on a DuPont 951 TGA coupled to a DuPont Instruments Thermal Analyst 2100. Viscosity measurements were performed at 25 °C in CH$_2$Cl$_2$ using a Ubbelohde type viscometer. GPC analyses were run on a Waters 490 equipped with RI and UV (254 nm) detectors, using THF as the solvent and polystyrene standard calibration.

Poly[(decanediyldioxybis(1,4-phenylene)bis(cyanomethylene))-*N,N'*-bis[*N*-*n*-propyladipamide]] (3a) was dried under vacuum at 50 °C overnight, 62% yield; $[\eta] = 0.36$ dL g^{-1} (CH$_2$Cl$_2$, 25 °C). IR (film): 2929, 2874 (al CH), 2240 (CN), 1654 (CO), 1612, 1512, 1409, 1250, 1178 cm^{-1}. ^{1}H NMR: δ 7.36 (d, 4H, ArH), 6.98 (d, 2H, CHCN), 6.93 (d, 4H, ArH), 3.97 (t, 4H, CH$_2$O), 3.17 (m, 4H, CH$_2$N), 2.44 (bs, 4H, CH$_2$CO), 1.74 + 1.60 + 1.46 + 1.32 (bs, 4H, CH$_2$), 0.81 (t, 6H, CH$_3$). GPC: $M_n = 10.0 \times 10^3$, $M_w = 18.7 \times 10^3$, $I_p = 1.9$. TGA (nitrogen): 5% weight loss at 338 °C. DSC: T_g at 36 °C. Anal. Calcd for DP$_n$ = 10 and acidic end groups ($M_n = 6535$): C, 72.05; H, 8.30; N, 8.71. Found: C, 72.03; H, 8.39; N, 8.59.

Poly[(decanediyldioxybis(1,4-phenylene)bis(cyanomethylene))-*N,N'*-bis[*N*-*n*-hexyladipamide]] (3b) was dried under vacuum at 50 °C for 5 h, 98% yield; $[\eta] = 0.46$ dL g^{-1} (CH$_2$Cl$_2$, 25 °C). IR (film): 2927, 2858 (al CH), 2240 (CN), 1657 (CO), 1613, 1512, 1411, 1250, 1178 cm^{-1}. ^{1}H NMR: δ 7.36 (d, 4H, ArH), 6.97 (d, 2H, CHCN), 6.91 (d, 4H, ArH), 3.99 (t, 4H, CH$_2$O), 3.20 (bt, 4H, CH$_2$N), 2.47 (bs, 4H, CH$_2$CO), 1.80 + 1.55–1.3 + 1.15 (36H, CH$_2$), 0.88 (t, 6H, CH$_3$). GPC: $M_n = 18.1 \times 10^3$, $M_w = 36.8 \times 10^3$, $I_p = 2.0$. TGA (nitrogen): 5% weight loss at 363 °C. DSC: T_g at −29 °C, T_m at 18 °C. Anal. Calcd for DP$_n$ = 12 and acidic end groups ($M_n = 8702$): C, 73.70; H, 9.01; N, 7.73. Found: C, 73.64; H, 9.10; N, 7.67.

Preparation of Polymeric Reissert Compounds by Condensation of Dialdehydes, Diamines, and TMSCN. Polymer 5a. To a solution of 1,10-bis(*p*-formylphenoxy)decane (**1**) (2.4602 g, 6.43 mmol) and 1.8 mL (13.5 mmol) of TMSCN in 10 mL of dichloromethane was added 0.9533 g (6.43 mmol) of Jeffamine EDR-148 in 2 mL of the same solvent. The mixture was stirred for 32 h, after which time it had become a viscous, orange solution. Dichloromethane (50 mL) was then added for dilution, followed by 4 mL (28.7 mmol) of triethylamine and, in 30 min, 2 mL (28.1 mmol) of acetyl chloride. The mixture was stirred for 20 h and poured into absolute ethanol. A gum was obtained, which was solubilized in 50 mL of dichloromethane and poured in 500 mL of ether. A very sticky yellow-brown gum was obtained, which was dried under vacuum at room temperature overnight and then at 40 °C for 4 h and 60 °C for 2 h. A light brown, translucent, film-forming polymer was obtained, 2.42 g, 59%; $[\eta] = 0.32$ dL g^{-1} (CH$_2$Cl$_2$, 25 °C). IR (film): 2930, 2856 (al CH), 2243 (CN), 1715 (weak), 1659 (CO amide), 1511, 1253 cm^{-1}. ^{1}H NMR: δ 7.35 (d, 4H, CH$_2$Ar), 6.9 (d, 6H, CH$_2$Ar + CHCN), 3.95 (t, 4H, CH$_2$OAr), 3.6–3.25 (m, 12H, CH$_2$O), 2.25 (s, 6H, CH$_3$), 1.8 (m, 4H, CH$_2$), 1.5–1.3 (m, 12H, CH$_2$). GPC: $M_n = 15.5 \times 10^3$, $M_w = 28.4 \times 10^3$, $I_p = 1.8$. TGA (nitrogen): 5% weight loss at 324 °C. DSC: T_g at 27 °C.

Polymer 5b. To a solution of 1,10-bis(*p*-formylphenoxy)decane (**1**) (5.364 g, 14.0 mmol) and 4.0 mL (30.0 mmol) of TMSCN in 30 mL of dichloromethane was added 1.63 g (14.0 mmol) of hexamethylenediamine in 20 mL of the same solvent. The mixture was stirred for 8 days. Dichloromethane (50 mL) was then added, and the solution was cooled over an ice bath. Triethylamine (5 mL, 35.9 mmol) and, in 15 min, acetyl chloride (3 mL, 42 mmol) were then added. The mixture was stirred for

30 min and poured into methanol (500 mL). A gum was obtained, which was solubilized in 50 mL of chloroform and poured into 500 mL of absolute ethanol. It was then solubilized in 50 mL of chloroform and poured into 500 mL of hexanes. A light yellow, sticky polymer was obtained, which was dried under vacuum at 45 °C overnight, 6.1 g, 73%, $[\eta] = 0.25$ dL g^{-1} (CH_2Cl_2, 25 °C). IR (film): 2932 (Ar CH), 2859 (al CH), 1655 (CO), 1612, 1514, 1406, 1251, 1178 cm^{-1}. GPC: $M_n = 6.9 \times 10^3$, $M_w = 15.0 \times 10^3$, $I_p = 2.15$. TGA (nitrogen): 5% weight loss at 352 °C. DSC: T_g at 52 °C, T_m at 75 °C.

Alkylation of Polymer 3a to Polymer 9. A solution of 0.40 g (1.27 mequiv of Reissert units) of polymer **3a** and 2 mL (9.4 mmol) of 1-iodododecane was dissolved in 10 mL of dimethylformamide (DMF). In the dark, 0.06 g (60% dispersion in oil, 1.5 mmol) of sodium hydride, rinsed with hexanes, was added, and the mixture was let stir in the dark for 30 h. The mixture was then poured into water, washed with methanol, taken up to 10 mL of DMF, and precipitated in water again. It was then rinsed with methanol, taken up in dichloromethane, and precipitated into hexanes. After 5 h of drying at 50 °C under vacuum, a yellow, amorphous polymer was obtained (0.30 g). Analysis by ^{1}H NMR spectroscopy showed an extent of alkylation of 30%. T_g was 24 °C.

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References and Notes

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