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Notes

A New Type of Poly(enamino nitrile) Analogous to Poly(phenyleneurea)

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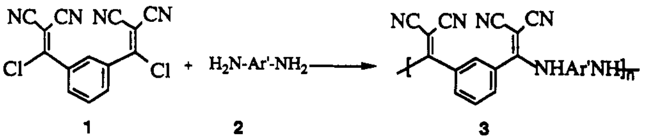
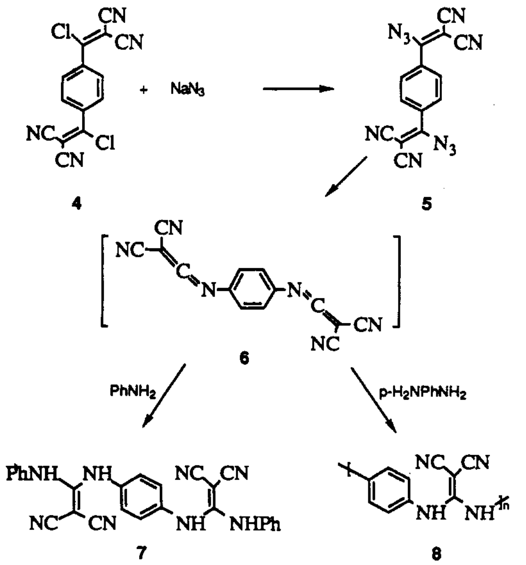
Introduction

Since poly(enamino nitriles) were synthesized first in 1986 by Moore and Robello,[1] a series of these polymers has been developed by the same group.[2] Poly(enamino nitriles) have excellent thermal stability and are superior to polyamides in terms of solubility and processability.

Up to now, all poly(enamino nitriles) have been prepared by one approach, vinylic nucleophilic substitution. For instance, poly(enamino nitrile) 3 was generated by treatment of *m*-bis(1-chloro-2,2-dicyanovinyl)benzene (1) with an aromatic diamine 2 in the presence of an acid acceptor such as 4-(dimethylamino)pyridine. This method was found to be effective, so far, for the preparation of all known poly(enamino nitriles); however, some poly(enamino nitriles) cannot be obtained by this approach. Our objective polymer, poly(*p*-phenyleneimino–enamino nitrile) 8, is one example where the previously described synthetic procedure cannot be employed because of the lowered nucleophilicity of arylamines.[3] A new method needed to be developed for the synthesis of this polymer.



In a previous paper,[4] we have demonstrated that *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (4) reacts with sodium azide, and the resulting *p*-bis(1-azido-2,2-dicyanovinyl)benzene (5) undergoes a double-barrel Curtius-type of rearrangement[5] to give the intermediate *p*-*N*,*N*′-bis(2,2-dicyanovinylidene)benzenediamine (6), which is trapped in situ with aniline to afford compound 7. Obviously, the latter contains a structural unit that is essentially identical with the repeat unit of a poly(enamino nitrile) 8. As a result, compound 7 serves as an ideal model for polymer 8. In this note we show that the approach used in the preparation of compound 7 can be extended to synthesize polymer 8. We also describe some of the new polymer's properties.



Results and Discussion

Poly(enamino nitrile) 8 was prepared by following the same method that we used to synthesize compound 7, with the exception that the intermediate bis(ketenimine) 6 was trapped in situ with *p*-phenylenediamine instead of aniline. A general procedure for the synthesis of poly(enamino nitrile) 8 is as follows: To a solution of 5 mmol of *p*-bis(1-chloro-2,2-dicyanovinyl)benzene in 30 mL of acetone was added a solution of 10.8 mmol of sodium azide in 15 mL of water at 0 °C with stirring. The mixture was allowed to stir at 0 °C for 0.5 h. After most of the acetone was removed by a stream of nitrogen, 50 mL of cold water was added to the mixture. A yellow solid was collected by suction.[6] The solid was then quickly dissolved in 25 mL of dimethoxyethane and dried with $MgSO_4$ at 0–5 °C for 2 h. The filtrate was treated with 5 mmol of *p*-phenylenediamine. The resulting mixture was gently warmed to 60–70 °C. A precipitate began to appear in the solution in a few minutes. After the mixture had been stirred at 60–70 °C for 1 h, the solvent was removed and the solid residue was washed thoroughly with hot methanol and THF and dried in vacuo for 20 h to give 64–75% of tan solid poly(enamino nitrile) 8. As is the case with most poly(enamino nitriles), polymer 8 was soluble in polar aprotic solvents such DMF, DMSO, and NMP. In accord with the proposed structure, it was also soluble in aqueous sodium hydroxide. Whereas all characterization parameters are in agreement with the proposed structure, the results of elemental analysis correspond to $C_{10.0}H_{6.4}N_{3.8}$, which is slightly off from the ideal repeat unit of $C_{10}H_6N_4$ of polymer 8, probably due to the hygroscopic nature of the polymer. The intrinsic viscosity of polymer 8, determined in DMSO at 24 °C (Ubbelohde viscometer), is 0.13 dL/g.

The IR spectra of polymer 8 and the model compound 7 are shown in Figure 1. The large water absorption band at 3400 cm^{-1} in the polymer illustrates the point made above about water absorption by polymer 8. While the model compound 7 shows two different cyano groups with stretching bands at 2190 and 2205 cm^{-1}, the polymer reveals only one cyano group with a stretching band at 2190 cm^{-1}, consistent with the structure of the repeat unit of the polymer and the structure of the model compound. Further evidence for the proposed structure is given by the following comparisons: (i) the intensity of the 820-cm^{-1} peak, a characteristic band for para-disubstituted benzene, has increased considerably in polymer 8 as compared with

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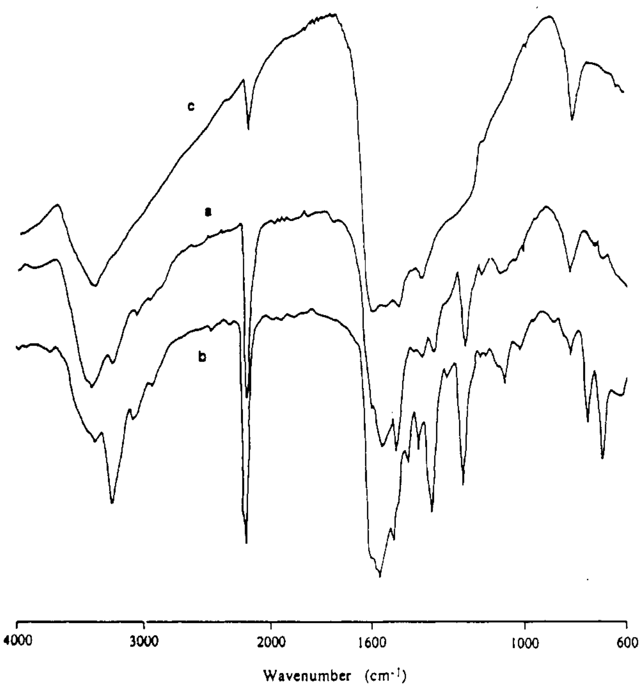


Figure 1. Infrared spectra of polymer 8 (curve a), model compound 7 (curve b), and polymer 9 (curve c), obtained after heat treatment of polymer 8.

that in compound 7 and (ii) as expected, the 690- and 750-cm^{-1} peaks, usually associated with monosubstituted benzene, do not appear in polymer 8 but are prominent in the model compound 7.

The UV spectrum of polymer 8 exhibits a maximum absorption at 328 nm, which is red-shifted with respect to that of the model compound 7 by 21 nm. The ^1H NMR spectrum of polymer 8 matches well the proposed structure with a typical broad chemical shift at ca. 7.2 ppm for the protons of the *p*-phenylene groups in the polymer. The protons of the corresponding phenylene group in compound 7 give a singlet with a chemical shift at 7.15 ppm.

Unlike most poly(enamino nitriles), polymer 8 exhibits only moderate thermal stability. The thermogravimetric analysis of polymer 8 shows mass loss beginning at ca. 270 °C under a nitrogen atmosphere (see Figure 2a), while most poly(enamino nitriles) are stable up to ~440 °C when heated at 10 °C min. Polymer 8 is more thermally stable than the corresponding poly(phenyleneurea).[7] The TGA of polymer 8 also indicates that it retains ca. 60% of its original mass upon heating to 800 °C.

The differential scanning calorigram of polymer 8 exhibits an endothermic peak at ca. 110 °C (see Figure 2b), which is believed to be its glass transition temperature. A glass transition temperature of 66 °C has been reported for a similar alkyl poly(enamino nitrile), poly(hexamethyleneimino–enamino nitrile).[3] Also observed in the DSC of polymer 8 is a broad exothermic peak centered at approximately 390 °C which does not reappear upon cooling and rescanning. On heating above that temperature, the resulting polymer was found to be insoluble in the solvents that dissolved polymer 8. The IR spectrum of the sample recorded after the above DSC experiment shows a decrease in the intensity of the cyano stretching band at 2210 cm^{-1} (see Figure 1a). This observation could be indicative of an intramolecular Hoesch-type cyclization at 390 °C,[8] where some of the enamino nitrile repeat units have rearranged to 4-aminoquinoline units, resulting in polymer 9.[9] A similar rearrangement has also been suggested in other poly(enamino nitriles).[1,2] Polymer 9 has an excellent thermal stability. The TGA of polymer 9 shows that it does not lose any mass until 580 °C and it retains nearly 80% of its original mass on heating to 800 °C (see Figure 2a, curve b).

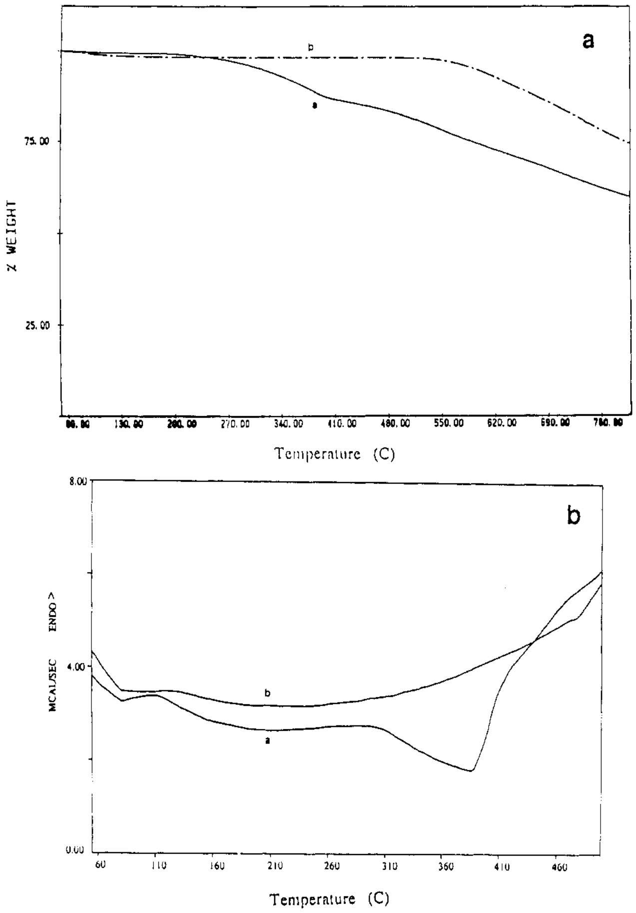
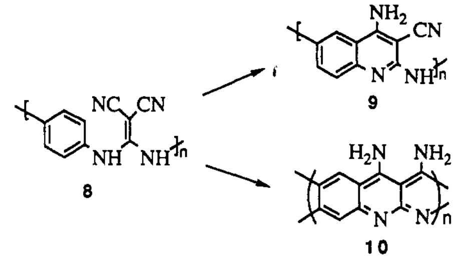


Figure 2. (a) Thermal gravimetric analysis (under nitrogen, heating rate 20 °C/min) of polymer 8 (curve a) and polymer 9 (curve b), obtained by holding polymer 8 at 400 °C for 5 min. (b) Differential scanning calorimetry (under nitrogen, heating rate 20 °C/min): curve a, polymer 8 to 500 °C; curve b, rescan of the curve a sample.



The expectation that polymer 8 might undergo a *complete* intramolecular cyclization at high temperature to yield the substituted poly(acene) [poly(benzonaphthridine) (**10**)] did not materialize because the cyano stretching band at 2210 cm^{-1} did not vanish on either prolonging the curing time or elevating the curing temperature. It is possible that admixture of certain Lewis acids may drive the cyclization to completion. On the other hand, reactions on polymers (particularly on the backbone) are notorious for not proceeding quantitatively.

Finally, it should be mentioned that because of the shock and friction sensitivity of organic azides, we never tried to isolate and purify bis(1-azido-2,2-dicyanovinyl)benzene (5). Thus it is almost impossible to maintain an exact stoichiometry between compound 5 and *p*-phenylenediamine, a crucial factor to achieve high molecular weight in this step-growth polymerization reaction.

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References and Notes

(1) Moore, J. A.; Robello, D. R. *Macromolecules* **1986**, *19*, 2667.

(2) (a) Moore, J. A.; Robello, D. R. *Macromolecules* **1989**, *22*, 1084. (b) Moore, J. A.; Mehta, P. G. *Polym. Mater. Sci. Eng.* **1989**, *60*, 74.

(3) Moore and Mehta have recently prepared an alkylenediamine analogue of polymer **8**, poly(hexamethyleneimino–enamino nitrile). Moore, J. A.; Mehta, P. G. *Polym. Mater. Sci. Eng.* **1990**, *63*, 351. We thank Professor Moore for information prior to publication.

(4) Shi, S.; Wudl, F. *J. Org. Chem.* **1988**, *53*, 5379.

(5) Friedrich, K. *Angew. Chem., Int. Ed. Eng.* **1976**, *15*, 261.

(6) *Caution*! Care must be taken to work with small quantities and never to allow the solid to dry completely. We have *never* had any problems at this stage; however, an explosion occurred at R.P.I. when a similar azide was dried. We thank Dr. D. R. Robello for private communication regarding that incident.

(7) For a detailed review, see: *Thermally Stable Polymers*; Marcel Dekker: New York, 1980.

(8) This is the simplest and energetically most favorable interpretation. It could also mean loss of the cyano functional group by some other unknown mechanism.

(9) The similarity of the IR spectra of polymers **8** and **9** speaks against a possible thermal transmogrification or carbonization.

Registry No. 4)(NaN_3)(p-H_2NPhNH_2) (copolymer), 132179-03-4.