Copolymers of 3,3',4,4'-Tetraaminobiphenyl and 1,2,4,5-Tetraaminobenzene with 1,1'-Bis(glyoxalyl)-ferrocene and 1,1'-Bis(phenylglyoxalyl)ferrocene

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Synopsis

Four monomers were synthesized and four copolymers prepared. The polymers were dark-colored, poorly soluble, crystalline products. The x-ray photographs were typical of triclinic crystals. The polymers degraded at temperatures lower than those characteristic of the analogous homopolymers. The recovered polymers were ferromagnetic.

INTRODUCTION

Two of many series of polymers with high thermal stability and low combustibility are the polyquinoxalines and the poly(phenylquinoxalines). Another is based on ferrocene. This latter series exhibits interesting electrical (semiconducting) and magnetic properties. It seemed of interest to combine the two structures in a copolymer as part of a continuing study of metallo-organic polymers.[1]

Metallocenes, including ferrocene, have been reviewed by Rosenberg,[2] metallocene polymers have been reviewed by Neuse and Rosenberg,[3] and ferrocene polymers, by Neuse.[4] The polymers described possess both pendent ferrocenyl groups and ferrocenylene groups in the chain backbone. It was the latter approach that was selected for our study, i.e. ferrocenylene groups in the chain backbone. Likewise, linear polyquinoxalines have been reviewed by Hergenrother.[5]

The literature relating to ferrocene polymers and to polyquinoxalines is extensive and need not be reviewed in detail. No literature on the alternating copolymer was found at the time of completion of this study,[6] but subsequently brief mention appeared in a patent.[7]

The polyquinoxalines are prepared by condensing an aromatic bisglyoxal with an aromatic tetraamine. In this case 1,1'-bis(glyoxalyl)ferrocene and 1,1'-bis-(phenylglyoxalyl)ferrocene were prepared to serve as the aromatic bisglyoxalyls. These heteroannular substitution products of ferrocene were condensed with 3,3',4,4'-tetraaminobiphenyl and 1,2,4,5-tetraaminobenzene in pairs thereby yielding four copolymers.

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0021-8995/79/0023-1601$01.00

EXPERIMENTAL

Synthesis of 3,3',4,4'-tetraaminobiphenyl (I) was by the procedure of Foster and Marvel[8] starting with recrystallized 4,4'-diaminobiphenyl. This was converted to the diacetamide,[8] nitrated,[9–11] hydrolyzed,[12] and reduced with stannous chloride in hydrochloric acid to yield the tetrahydrochloride which was stored and then converted to the free tetraamine with dilute sodium hydroxide in a nitrogen atmosphere for use.

Synthesis of 1,2,4,5-tetraaminobenzene (II) was accomplished similarly from 1,3-diaminobenzene using a different hydrolysis technique.[13] The 1,1'-bis-(glyoxalyl)ferrocene (III) was prepared by treating ferrocene with more than two equivalents of acetyl chloride or acetic anhydride in the presence of aluminum trichloride.[14] The product, 1,1'-diacetylferrocene, with very small amounts of the homoannular or asymmetrical product (1,2-diacetylferrocene),[15,16] was oxidized with selenium dioxide[17] using the technique described by de Gaudemaris and Sillion.[18] The product was recovered as the hydrate.

A similar procedure was used to prepare 1,1'-bis(phenylglyoxalyl)ferrocene (IV) from phenylacetyl chloride by oxidizing the intermediate 1,1'-bis(phenylacetyl)ferrocene with selenium dioxide. Since both aldehydic hydrogens are substituted, this compound may be better named 1,1'-bis(phenyldiketo)ferrocene. The structures of the intermediates and products were confirmed by infrared analyses and melting points.

Condensation of 3,3',4,4'-tetraaminobiphenyl (I) (recrystallized before use) with 1,1'-bis(glyoxalyl)ferrocene dihydrate (III) yielded copolymer I–III. To the tetraamine in redistilled dry dimethylformamide was added the glyoxalyl compound in the same solvent, and the solution heated to 120°C for 1 hr and then refluxed for 4 hr, all under a nitrogen blanket. The product, typically black flakes, was separated by decantation and, washed with dimethylformamide, water, ethanol, and finally dimethyl ether. The product was dried first in vacuo, then at 150° in an oven under a nitrogen blanket. The yield was almost complete, and elemental analysis was as predicted. The product was also prepared in m-cresol solution:
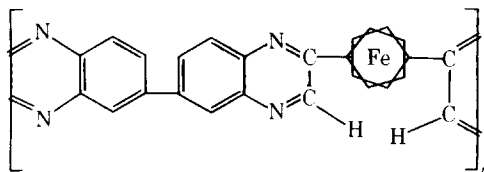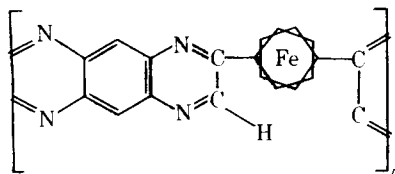

copolymer I–III

Condensation of 3,3',4,4'-tetraaminobiphenyl with 1,1'bis(phenyldiketo)ferrocene dihydrate yielded copolymer I–IV by the same procedure, by heating slowly to 100° and then at 200° for 16 hr. The yield was almost complete. The product was separated, washed with water and ethanol, and dried overnight in vacuo. Elemental analysis was as predicted. The product was slightly soluble in m-cresol:
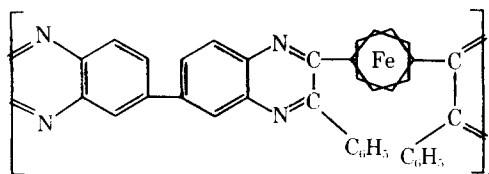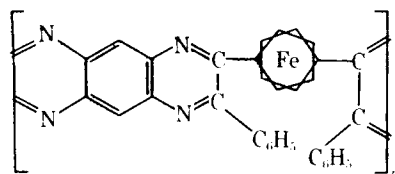
copolymer I–IV

Condensation of 1,2,4,5-tetraaminobenzene with 1,1′-bis(glyoxalyl)ferrocene dihydrate yielded copolymer II–III similarly by heating for 4 hr at 200°. The product was separated, washed, and dried as above. Elemental analysis was as expected:

copolymer II–III

Condensation of 1,2,4,5-tetraaminobenzene with 1,1′-bis(phenyldiketo)ferrocene yielded copolymer II–IV by the same procedure. Elemental analysis was as expected:

copolymer II–IV

The four copolymers were dark brown to black, shiny platelets, infusible, and hard. No attempts were made to prepare terpolymers or multipolymers which might have been softer and more flexible.

RESULTS AND DISCUSSION

The dark-colored, hard polymers were insoluble in water and most organic solvents, cold or hot. Polymers I–III and I–IV were slightly soluble in m-cresol; polymer II–III, in carbon tetrachloride; and polymer II–IV, in chloroform and dimethylformamide. All of the polymers were partially or completely soluble in strong acids, sometimes with decomposition and with a change to lighter colors. The insolubility of the polymers is not unexpected; it is perhaps related to some crosslinking but more likely due largely to the presence of the high-melting crystals.

Finely ground specimens were tested for crystallinity using a Philips instrument, Debye Scherrer camera, and $K_\alpha Cu$ radiation. Typical rings of highly crystalline materials are obtained with the powder, and triple lines indicated triclinic system. There was no evidence of amorphous halos. The EPR spectra of the polymers were consistent with the expected structures, i.e., completely conjugated ring systems.

A Stanton Thermobalance was used to obtain the thermogravimetric data in Figure 1. Polymers I–III and I–IV decomposed rapidly at about 350°C in air (curves a and c). Polymer I–III decomposed somewhat more slowly at high temperatures in argon (curve b). Copolymers II–III and II–IV were stable to higher temperatures, about 400°C; and a stable residue amounting to a substantial fraction of the total weight remained at the highest temperature reached (curves d and e).

The polyquinoxalines and poly(phenylquinoxalines) as well as the polyferrocenes have been reported to be thermally stable to 500°C or higher. However, the incorporation of the ferrocene unit into the chain reduced the thermal stability. A similar observation was made by Mulvaney, Bloomfield, and Marvel,[19] who noted reduced stability of a poly(benzborimidazoline from 3,3',4,4'-tetraminobiphenyl and 1,1'-ferrocenylenediboronic acid when compared with the phenylene analog. The residues from polymers I–III and I–IV corresponded almost exactly to the iron oxide residue one would expect. However, the residues from polymer II–III and II–IV were not similar to iron oxides and appeared to be highly thermally stable products amounting to about half of the original weight. The black, stable products were not further characterized. In no case was a melting point reached, nor was there any evidence of a loss of volatile impurities such as solvents or unreacted monomers. The presence of the pyrazine hydrogen did not contribute to oxidizability since the phenyl-substituted ring was not more stable.
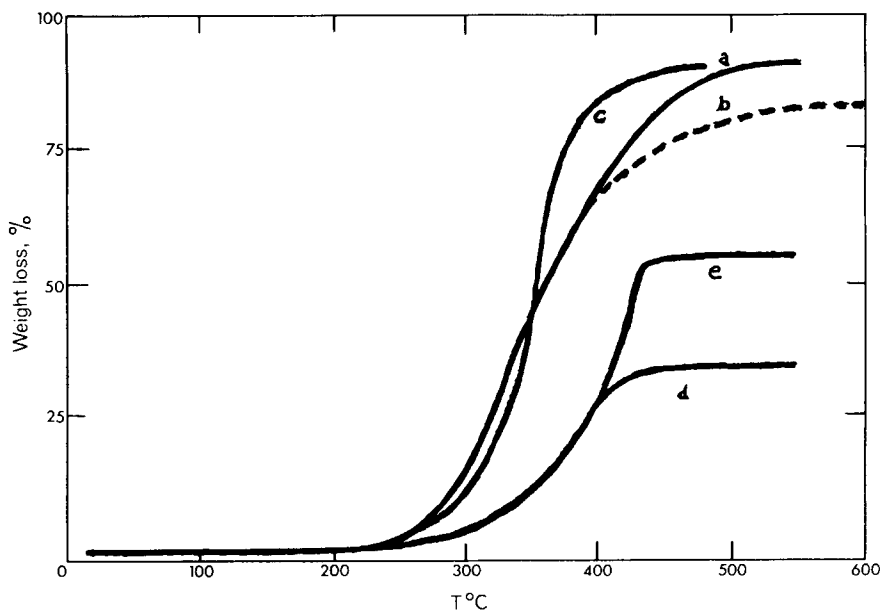

Fig. 1. Weight loss vs. temperature: (a) copolymer I–III in air; (b) same under argon; (c) copolymer I–IV in air; (d) copolymer II–III in air; (e) copolymer II–IV in air.
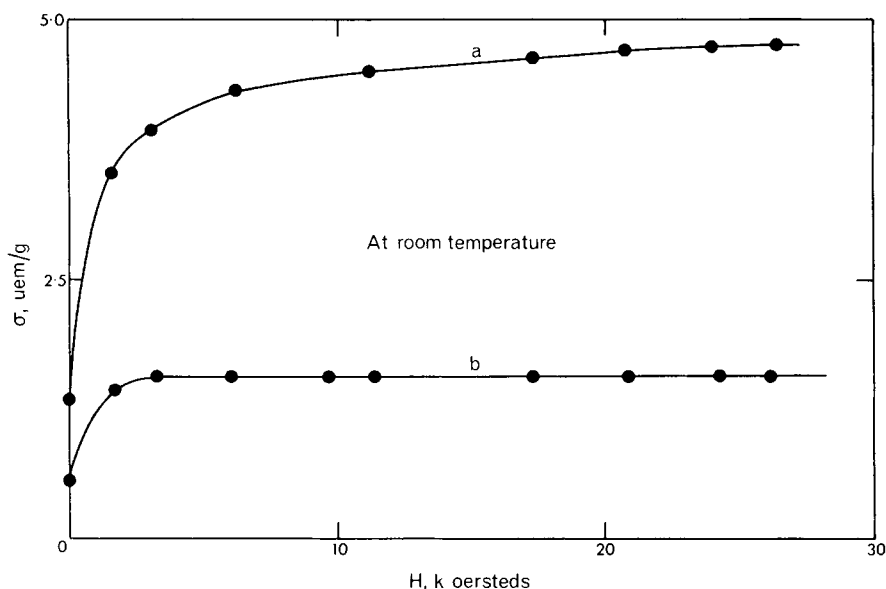
Fig. 2. Magnetization vs. magnetic field strength: (a) copolymer I–III; (b) copolymer I–IV.

Many ferrocene-containing polymers exhibit magnetic properties.[2,3,20–22] The crystalline products, as formed, gathered at the ends of the Teflon-coated stir bars, and each particle seemed to be like an iron filing. Orientation in a magnetic field seemed to be easier for polymers II–III and II–IV than for polymers I–III and I–IV. The primary difference in structure between the two series is the longer distance between iron atoms in the latter pair, i.e., the polymer chains can be considered as segments linked by iron atoms and the segment lengths would be the same and longer for the two polymers based on monomer I and the same and shorter for the two based on monomer II, ignoring small effects due to cis and trans forms and steric strain from the phenyl group of monomer IV.

The magnetic properties of the two polymers based on 3,3′,4,4′-tetraamino-biphenyl are in Figure 2. Magnetization as a function of applied field indicates a higher plateau for polymer I–IV than for I–III. Saturation took place at 1.5 emu for copolymer I–III and at approximately 4.5 emu for copolymer I–IV. The saturation values were equal to about 2.5% of those for iron. This suggested that, in the crystalline regions, the iron atoms were ordered to form a Weiss domain. Free iron was not present in the starting materials, and all reaction steps were conducted in an inert atmosphere. The products decomposed before a Curie temperature was reached. Magnetic properties were exhibited while the polymer was forming in the inert atmosphere of the reaction flasks and prior to any possible degradation during drying.

In general, it has been observed[20] that ferrocene was diamagnetic but that the polymers were paramagnetic particularly as the molecular weight increases. The effect was more pronounced the closer together the iron atoms were, and the effect was accentuated by heating to 120°C. Dulov et al.[23] have suggested that iron-organic compounds formed on pyrolysis above 250°C could be the source of the ferromagnetic properties observed with degraded polymers. It is possible that ferromagnetic iron-organic compounds were formed similarly during

polymerization and exhibited the properties noted by virtue of the closely packed, crystalline nature of the polymers.

However, it is uncertain whether the magnetic properties are intrinsic or extrinsic, although the latter is probably excluded on a quantitative basis when both magnetization and the x-ray data are considered. Likewise, while care was taken to exclude iron and oxygen during the preparations and excessive heating was avoided, the formation of ferricenium sites, particularly on exposure to oxygen, cannot be excluded. For a more detailed discussion of this complex problem, see the review by Neuse and Rosenberg, pages 39–44.[3]

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