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SYNTHESIS OF 2-(p-AMINOPHENYL)OXAZOLINE AND ITS CATIONIC POLYMERIZATION STUDIES BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The monomer 2-(4-aminophenyl)oxazoline has been prepared in good yield and briefly investigated for cationic, homopolymerization and copolymerization characteristics, using 2-ethyloxazoline as a comonomer. Cationic polymerizations can be conducted to producesoluble poly[2-(4-aminophenyl)oxazoline] and poly[2-(4-aminophenyl)-oxazoline-co-2-ethyloxazoline].

INTRODUCTION

2-Substituted oxazolines and oxazines have received considerable attention in recent years for the production of both chain-growth and step-growth polymers and/or thermosets [1-2]. Oxazolines and oxazines belong to a class of compounds known as cyclic imino ethers, which are substantially stable but undergo ring-opening reactions with carboxylic acids, phenols, thiophenols, amines, isocyanates, epoxides, alkyl halides, etc., giving adducts with no chemical fragments production

[3]. Oxazoline moieties are known to promote adhesion to a variety of surfaces [3]. Considering the latter and other factors, oxazoline functionalized monomers and polymers are believed to be highly versatile for a wide spectrum of applications, such as the design of improved coatings and adhesives, composites, specialty chemicals for pharmaceuticals, chemicals for the paper and textile industries, polymeric compatabilizers, etc. [2].

As part of a project associated with preparing and evaluating new cyclic imino ether functionalized monomers for coatings and adhesives applications, we have had the occasion to prepare and characterize 2-(4-aminophenyl)oxazoline (APO). Amino group functionalized oxazolines and oxazines belong to a family of bireactive compounds which possess interest in both theoretical research and practical applications. The monomers 2-(2-aminophenyl)oxazoline [4], 2-(3-aminophenyl) oxazoline [5], and 2-(4-aminophenyl)-oxazoline [6, 7], which have received very little attention in the literature, have had no polymerization study as AB type monomers. However, some attention has been given to using bisoxazolines and diamines for the production of thermosetting materials [8, 9]. In this communication, we report on the high yield synthesis of the novel bireactive AB monomer APO, using the raw material p-aminobenzonitrile, via a simple one step reaction of the nitrile with excess ethanolamine. We also report our preliminary findings concerned with the homo- and copolymerization of APO with other oxazolines, such as 2-ethyloxazoline, using differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

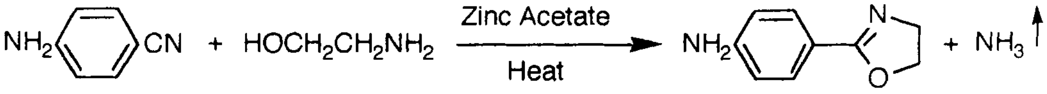
Unless specified, reagent grade chemicals and solvents were used as received from chemical suppliers: p-Aminobenzonitrile (ABN, Aldrich), ethanolamine (EA, Fisher Scientific), 2-ethyloxazoline (2EO, Aldrich), and methyl p-toluene sulfonate ($TsOCH_3$, Aldrich). Zinc acetate dihydrate (Aldrich) was dried by heating at 125°C for 4 hours before use.

Characterization

The ^1H NMR spectra were obtained on a 250 MHz Bruker AM spectrometer, using deutrated chloroform or DMSO as a solvent, with TMS as internal standard. FT-IR spectra were obtained on a MIDAC spectrophotometer. Thermal analyses were performed by differential scanning calorimetry (TA Instruments, DSC 910) and thermomechanical analyzer (TA Instrument, TMA 2940). Melting points, uncorrected, were determined by DSC and use of an Electrothermal Melting Point Apparatus.

Monomer Preparation

2-(4-Aminophenyl)oxazoline, APO, was prepared as follows:



p-Aminobenzonitrile (ABN), 59 g (0.5 M) was combined with ethanolamine (EA), 61 g (1.0 M), i.e., in a molar ratio of ABN / EA equal to 1/2, together with 3 wt% zinc acetate and 200 ml of xylenes in an appropriate 3-neck round bottom flask fitted with a thermometer, condenser, nitrogen gas inlet tube, magnetic stirrer, and ammonia gas receiver. The mixture was heated with moderate stirring at the reflux temperature of xylenes (130-137°C) under a nitrogen blanket for 29 hours or until no ammonia was detected in the off gas. After distilling off a substantial amount of the xylenes, the reaction mixture was poured, with vigorous stirring, into a large volume of water-ice mixture. The crude product was collected by filtration, washed with distilled water and dried under vacuum. The solid product, 82% yield, was purified by recrystallization from acetonitrile, giving white, needle-like crystals with m.p. 165-167°C (158-160°C [6]).

Polymerizations

The cationic homopolymerization of APO was examined by DSC. APO (15.1 mg) and 1.1 mg of $TsOCH_3$ initiator were placed in an aluminum DSC pan and the pan hermetically sealed with an aluminum cover. Polymerization of the sample was monitored by DSC while heating under nitrogen at a rate of 5°C/min from 50-250°C. A second DSC scan was performed on the polymerized sample at a heating rate of 20°C /min. The homopolymerization of APO was also carried out in a small glass vial at the same monomer to initiator ratio. After sealing under nitrogen, the sealed glass vial and its contents were heated overnight over the temperature range 160-170°C. A clear, yellow, glassy solid polymer was obtained, which would only dissolve in strong polar solvents such as dimethyl sulfoxide (DMSO) and N,N-dimethylformamaide(DMF). In contrast, APO was soluble in chloroform and tetrahydrofuran without difficulty. The polymer product was

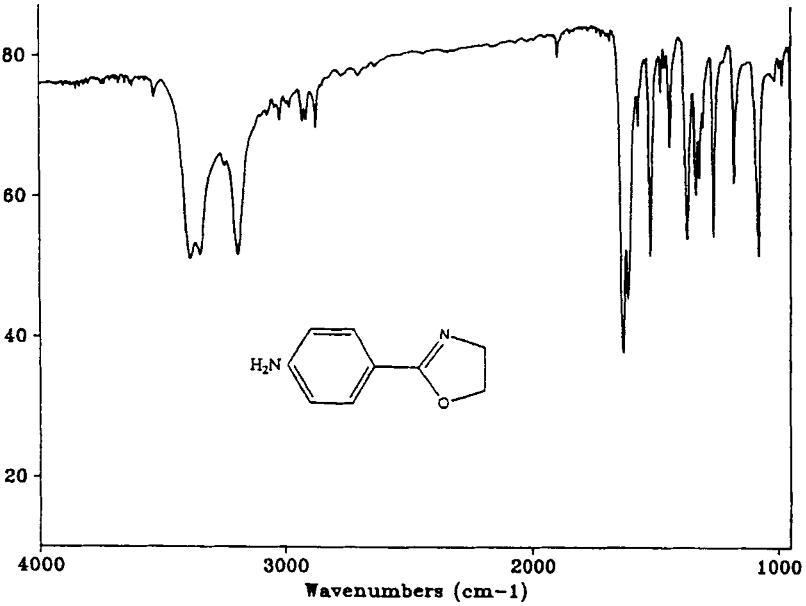


Figure 1. FT-IR spectrum of 2-(4-aminophenyl)oxazoline (APO).

purified by dissolving in DMF and precipitation with chloroform. The recovery of purified polymer was >96%.

The cationic coploymerization of APO with 2-ethyloxazoline (EO) was briefly examined. APO, at either the 10% or 20% level, was dissolved in 2-ethyloxazoline at 70°C in a small glass vial, along with 1.0% $TsOCH_3$ initiator. After purging with nitrogen, the vials were sealed. The mixtures were then heated for 20 hours at 120-130°C. The slightly yellowish solid products, which were optically clear and brittle in nature, were soluble in water and other polar organic solvents. The copolymers were purified by dissolving in chloroform and precipitating with ether. The white powder products were obtained in yields of >95%. For comparison, poly(2-ethyloxazoline) polymer was prepared from its liquid monomer under the same condition as the above copolymers.

RESULTS and DISCUSSION

The FT-IR spectrum of monomer APO is shown in Figure 1, with a strong peak at 1628 cm^{-1}, confirmed the presence of the -C=N- stretch for the oxaz-

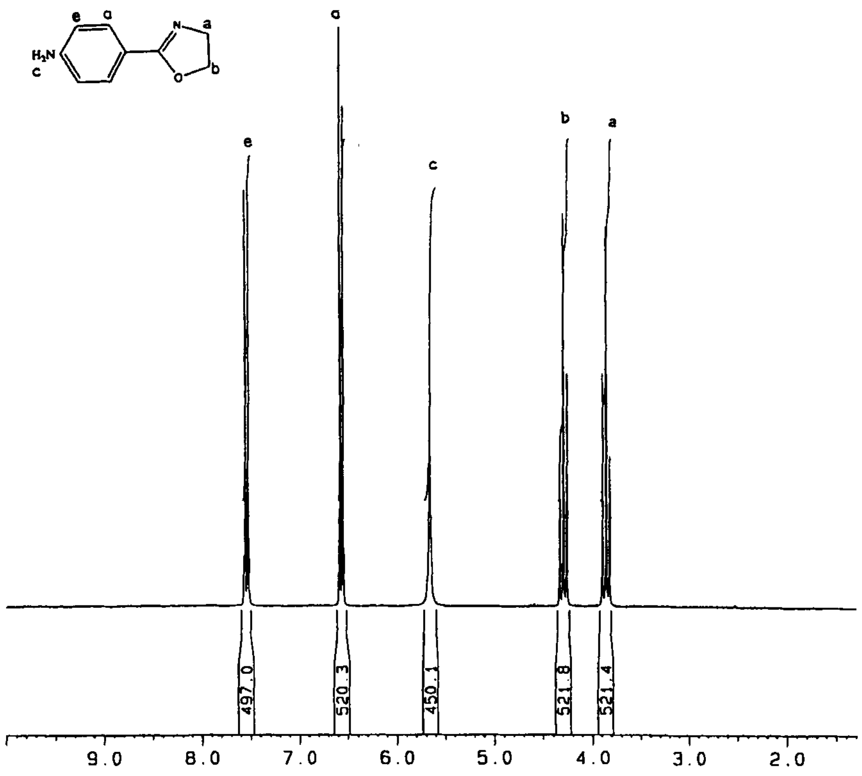


Figure 2. ^{1}H NMR of APO monomer in DMSO.

oline ring. The aromatic amino group showed a doublet at 3500 cm^{-1}. The ^{1}H NMR spectrum (Figure 2) also confirms the structure.

DSC studies of the homopolymerization of APO are shown in Figure 3. The polymerization enthalpy (ΔH) obtained for the polymerization was 34 KJ/mol, with a sharp exotherm peak at a maximum polymerization temperature of 165°C (curve a, Figure 3), which is located at the melting temperature for the monomer. A second DSC scan for the polymerized system showed the monomer completely polymerized, i.e., no exotherm was observed, and a glass transition temperature (T_g) was evident at 3164.8°C (curve b). The APO monomer cationically polymerized in a small glass vial exhibited an identical T_g at 164.9°C by DSC. When the cationic initiator was eliminated, no polymerization occurred upon heating, as shown by DSC (curve c). The sharp endotherm peak on curve c shows the melting point of APO. The polymer undergoes oxidative attack at temperatures $\geq$236°C, decomposing into a dark colored, ash-like material. Since both the amino and the

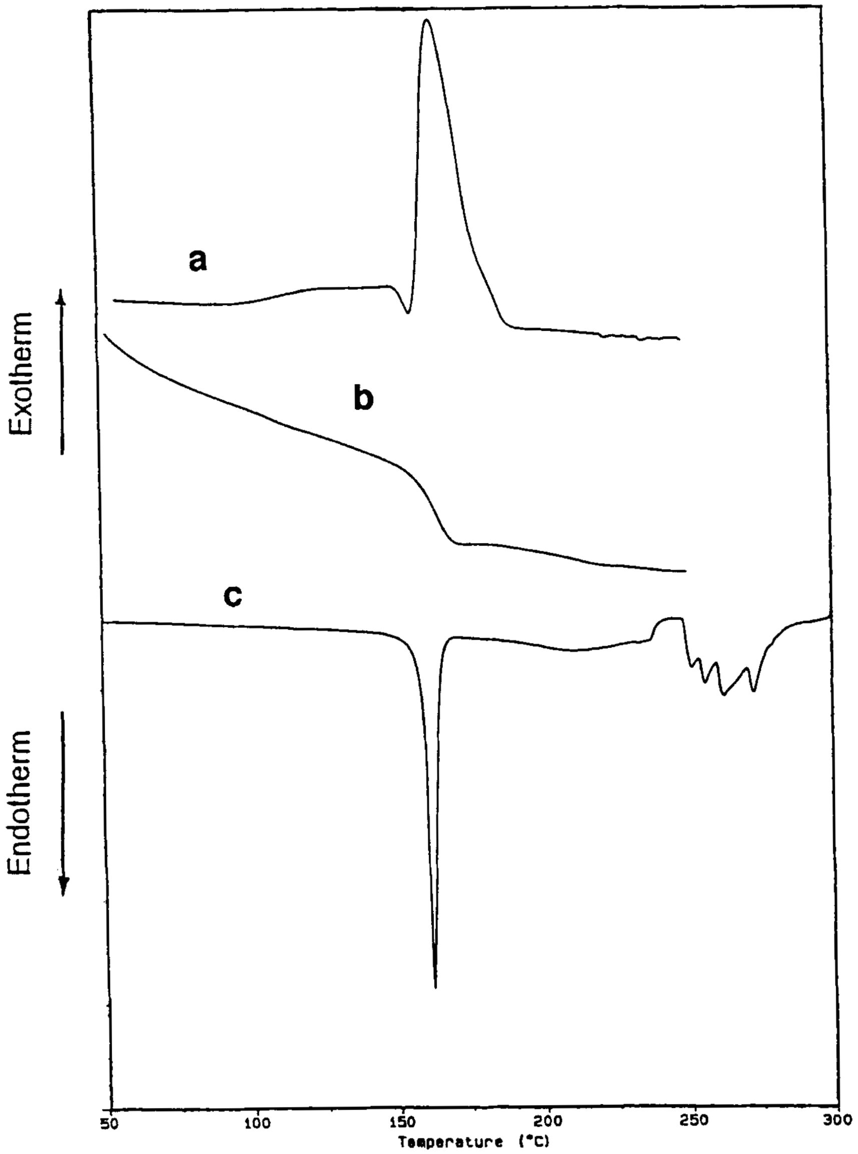


Figure 3. DSC studies on APO monomer:
(a). Thermogram of APO cationic polymerization (a);
(b). Thermogram of poly(APO) b;
(c). Thermogram of APO monomer upon heating without initiator

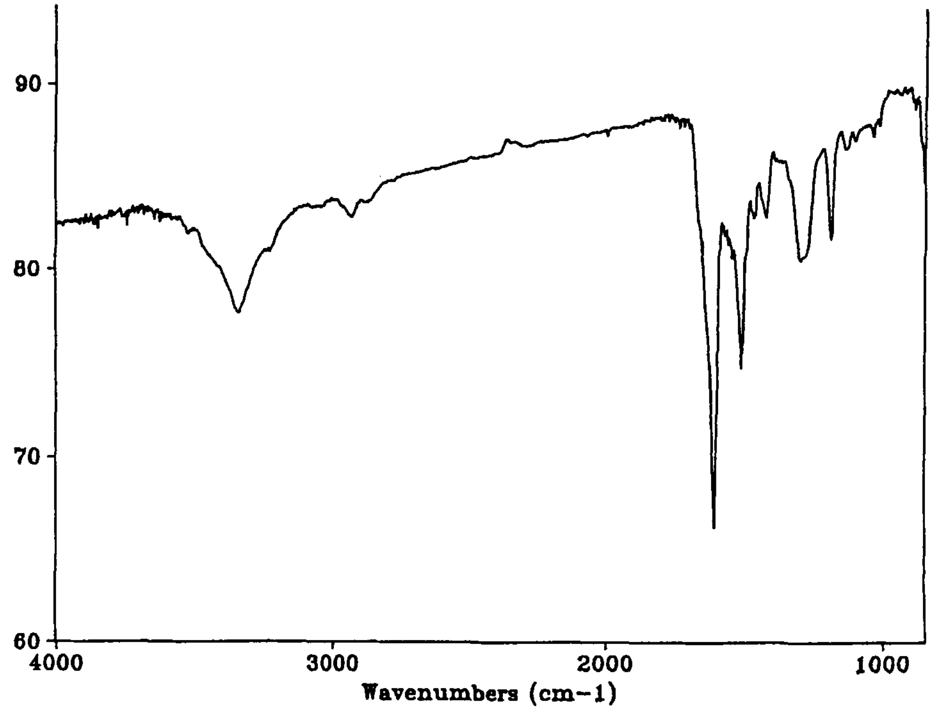
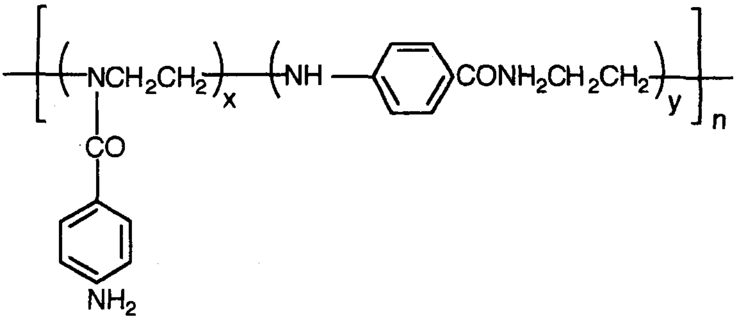


Figure 4. FT-IR spectrum of poly(APO) homopolymer.

oxazoline group are basic in nature, one would expect that both could or would participate in cationic polymerization. Figure 4 shows the FT-IR spectrum of poly[2-(4-aminophenyl) oxazoline]. A strong C=O stretch band was located at 1607 cm^{-1} and an N-H stretch band at 3343 cm^{-1}. Combined with the ^{1}H NMR spectrum (Figure 5), a structure for the cationically polymerized APO monomer was postulated to contain the following residues:



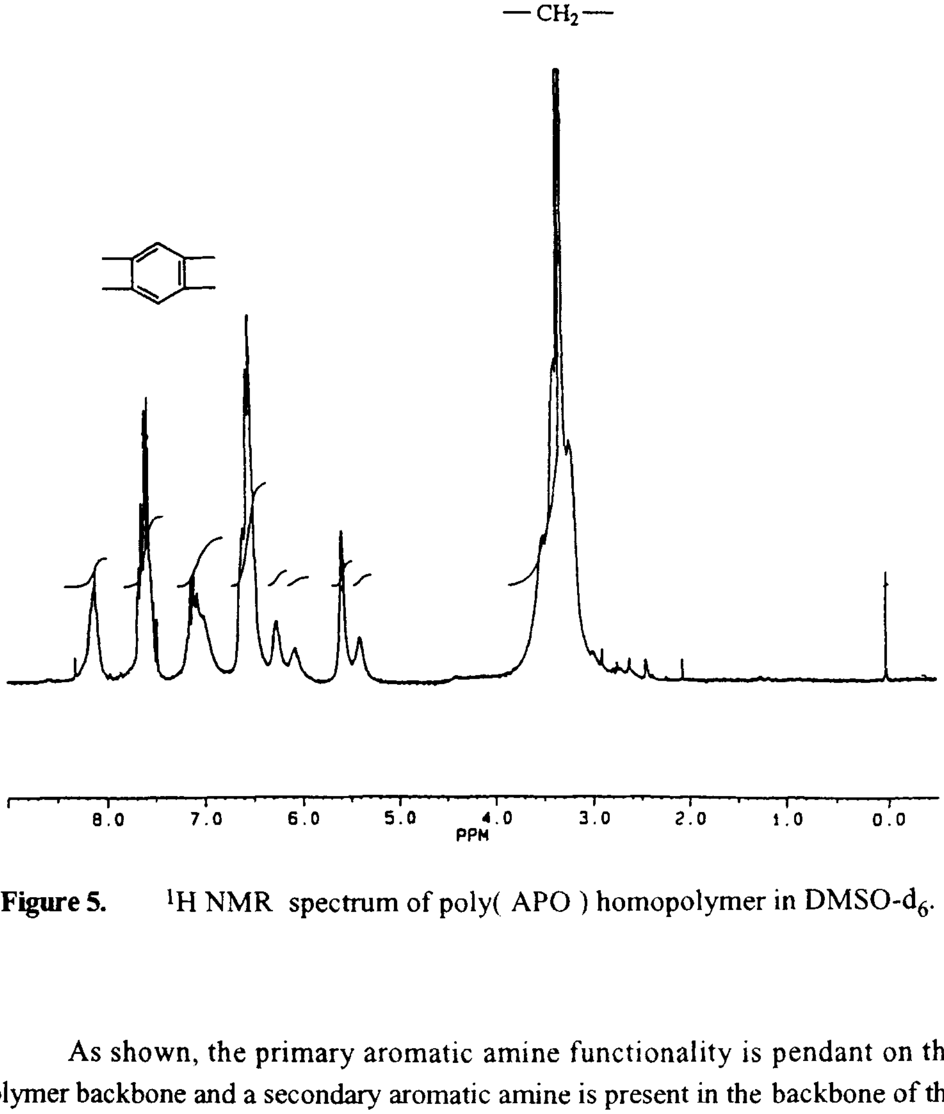
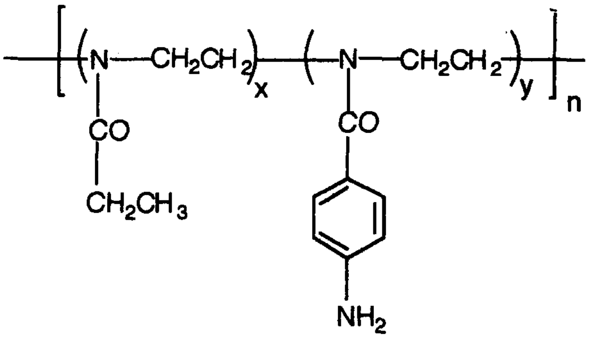


Figure 5. ^{1}H NMR spectrum of poly(APO) homopolymer in DMSO-d_6.

As shown, the primary aromatic amine functionality is pendant on the polymer backbone and a secondary aromatic amine is present in the backbone of the polymer. This proposed structure is in harmony with studies conducted by others concerned with the reaction of amines with oxazolines [10] and the cationic copolymerization of bisoxazolines with aromatic diamines [8, 9].

The optically transparent copolymers of APO with 2-ethyloxazoline, having the envisioned or simplified structure shown below. were readily soluble in water, within the composition range studied.

The APO-2EO cationic copolymeization route provides a path to some very unique, water soluble copolymers, which may be useful for curing epoxy resins and other reactions of interest. For example, we found that the APO:2EO (20:80, wt:wt) copolymer composition formed a thermoset with epoxy resins upon



heating a mixture of the materials at 110°C for several hours. The amino group was easily observed and monitored in the reaction mixture, using FT-IR, as well as being detected in the spectrum of the product. Using DSC and TMA analysis, with heating rates of 20°C for DSC and 10°C for TMA, it was observed that the T_g for the cured products increased with increasing amounts of the APO copolymer used to cure the epoxy resin, which would be expected.

Poly(2-ethyloxazoline), prepared in this effort, was observed to have a T_g of 57.3°C by DSC and a T_g of 54.2°C observed by TMA, along with a polymer melt temperature (PMT) of 78.0°C, as shown by TMA. Water soluble poly(2-ethyloxazoline) is reported [11, 12] to have T_g = 70°C. The APO:2EO (90:10, wt:wt) copolymer had T_g's at 63.0°C, as shown by DSC, and 66.8°C, as shown by TMA, followed by a PMT of 100.3°C, as shown by TMA. The APO:2EO copolymer with a 80:20 (wt:wt) ratio had a T_g of 72.3°C, as shown by DSC.

CONCLUSION

Polyoxazolines with pendant aromatic amino groups are unique functionalized compositions, having utility to prepare a wide variety of thermosetting materials. We believe that polymeric materials of the type described should be useful for curing epoxy resins to provide new formulations for coatings and adhesives. Further, polymeric materials described herein should open up many new avenues for discoveries in polymer blends and alloys, along with studies on new interpenetrating polymer network (IPN) systems, since it is well documented that poly(2-oxazolines) are miscible with a variety of commodity polymers [12]. Such concepts will be focused on in future communications.

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