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COMPATIBILIZATION OF POLYPHENYLQUINOXALINE WITH OTHER POLYMERS USING CHLOROFORM AS THE SOLVENT IN THE PREPARATION OF POLYMERIC MEMBRANES

BY ISAAC ANGRES

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16 NOVEMBER 1977

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This work was performed to determine if polyphenylquinoxaline (PPQ) can be made compatible with other polymers such as polyvinylacetate, polyvinylpyrrolidone, vinylpyrrolidone/vinylacetate copolymer, cellulose acetate, cellulose triacetate, and polybrene. The primary purpose was to prepare homogeneous solution blends containing PPQ combined with one, two or three of the above polymers. Such solution blends were used to prepare polymeric membranes to be used as battery separators.

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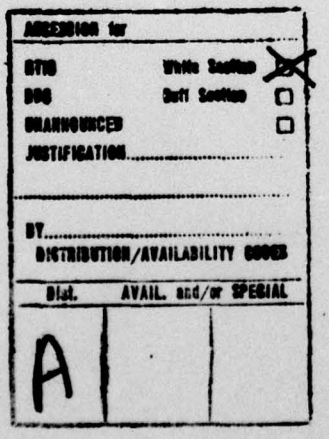
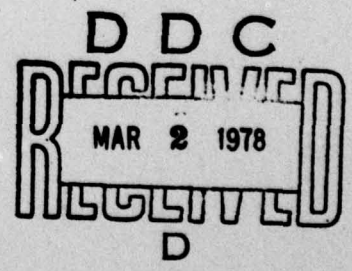
SUMMARY

This investigation was undertaken to develop a method of compatibilizing polyphenylquinoxaline (PPQ) with polymers such as polyvinylpyrrolidone (PVP), cellulose acetate, cellulose triacetate, polyvinyl acetate and polybrene. Such compatibilization is achieved by using chloroform as the solvent and the resulting blends are used for preparing membranes useful as battery separators. This work is being performed under NAVSEA Task Number SF43431302.

J. R. DIXON
By direction





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INTRODUCTION

Earlier investigations[1] on the development of polymeric membranes based on polyhenylquinoxalines (PPQ), had as the leachable additive polyvinylpyrrodidone and m-cresol as the solvent. However, the use of m-cresol as the solvent is somewhat cumbersome because of its high boiling point. In addition, when the need to use other leachable additives arose, we encountered a problem of polymer-polymer compatibilization when m-cresol was used as the solvent.

It is known that the unique characteristics of homopolymers and copolymers are conferred by their specific chemical and stero-structures, by their molecular weight distribution, and by their intra- and inter-chain interactions. Although such homogeneous materials have numerous useful chemical and physical properties, it is often desirable to seek improvements (i.e., lower their inherent electrical resistance) in their characteristics or processing requirements. In order to accomplish the above improvements one finds that it is necessary to prepare multicomponent polymer systems. Thus, homogeneous blends (in solution) comprising mixtures of polymers, provide a route to combinations of properties not otherwise available.

In this study our efforts focused on the preparation of homogeneous solution blends in chloroform. The above blends contain PPQ as the main polymer and other resins such as polyvinylacetate, polyvinylpyrrolidone, vinylacetate/vinylpyrrolidone copolymer, cellulose acetate, cellulose triacetate, and polybrene (a diquatemary ammonium bromide polymer). The use of chloroform as the solvent solves the problem of PPQ compatibilization with other polymers in m-cresol. Similarly, it will be noted that preparation of the membranes is faster because of the ease of evaporation of the solvent.

EXPERIMENTAL

POLYMER PREPARATION

Poly-2,2'-(p.p'oxydiphenylene)-6.6'-Di(3-phenylquinoxaline)

The PPQ based polymer used in the preparation of the membranes for this study was purchased as a 10% solution in m-cresol from the Narmco Division of the Whittaker Corporation. The synthetic route to prepare this polymer is as follows:

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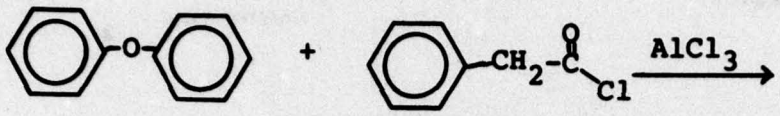
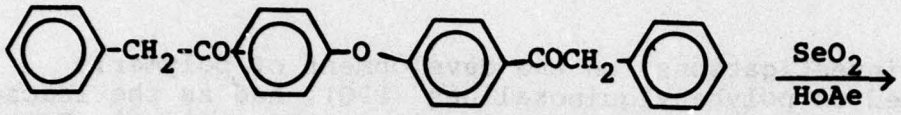
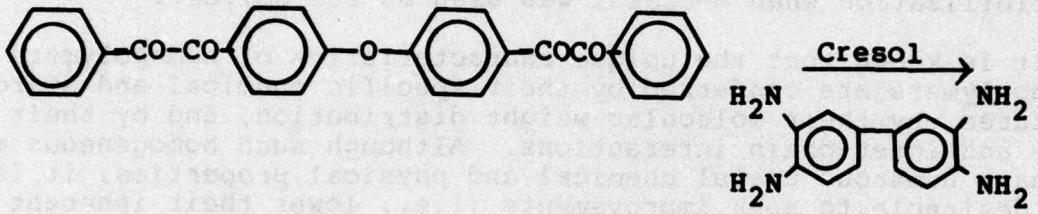
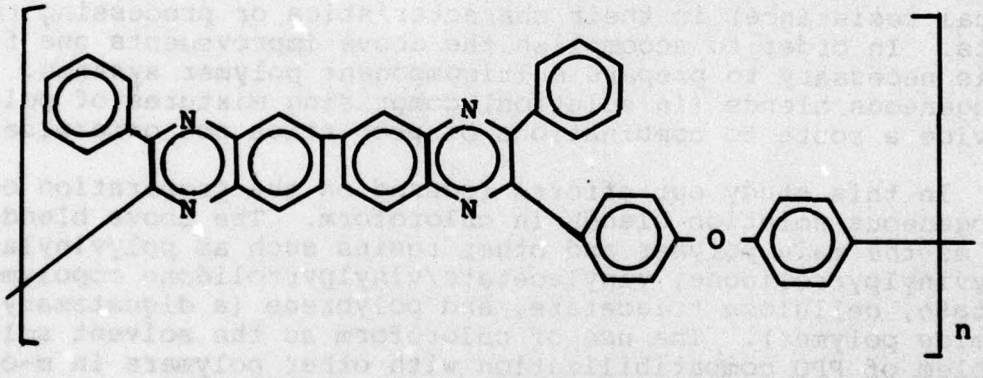
1. W. P. Kilroy and J. V. Duffy, "Development of an improved separator Material for Alkaline-Silver-Zinc batteries', NSWC/TR-76-135 White Oak, Maryland, February 1977.









The reported inherent viscosity for this polymer is 2.05 $\frac{dl}{g}$ and the glass transition temperature is 693°K (420°C)[2]. Polyvinylacetate (low, medium, and high molecular weight), polyvinylacetate/vinyl pyrrolidone copolymer, polybrene, polyvinylpyrrolidone, cellulose acetate, and cellulose triacetate were all obtained from Aldrich Chemical Company.

MEMBRANE PREPARATION

The following procedure applies to all of the above polymers, when blended with the PPQ and using chloroform as the solvent:

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2. P. Hergenrothen and H. Levine, J. Polymer Science A-1 5 1453(1976)

30 g of the 10% PPQ solution is added to a suitable container followed by 2 g of any of the above polymers or 2 g of a mixture of the above polymers. To the above mixture there is added 100 ml of chloroform and the resulting compositon is stirred thoroughly until a homogeneous solution is obtained. The homogeneous solution is used for casting purposes.

The membranes are prepared by spreading the homogeneous solution onto a glass plate (16 cm X 28 cm X 0.9 cm) with a metal bar. The thickness of the final film was controlled by means of masking tape which was placed along the edges of the glass plate (3 layers of tape ≈ 1 mil thickness). It was found necessary to thoroughly wash the glass plate with water and detergent and then to rinse with isopropyl alcohol to insure good wetting by the polymer solutions.

Following the casting of the film, the solvent (chloroform) is allowed to evaporate slowly for about 2-3 minutes by partially enclosing the plate with a plastic container, and then immersing the plate in a 50:50 methanol-water bath, and allowing to stand for 10 minutes. The film is washed with water and dried in air. Films obtained by this method have good handleability and do not shrink on drying.

The leachable additives are either extracted with water or hydrolyzed in KOH (45%) at 80°C to create porosity. (The full characterization and the effect of hydrolysis on resistance will be the subject of another report to be published at a later date).

DISCUSSION

Incompatibility (insolubility) is an often encountered problem that prevents the preparation of useful blends. The use of chloroform as the solvent allows for the preparation of many and useful PPQ polyblends in solution. A plausible explanation as to why chloroform acts as a good compatibilizing agent is accounted by weak hydrogen bonding with the PPQ, as shown in Figure 1.

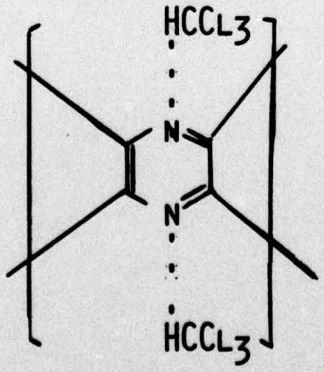

Figure 1. Hydrogen-bonded Interaction of PPQ with Chloroform.

By tying up all the PPQ by means of this hydrogen bonding interaction one can then dissolve other polymers in the same system without encountering the problem of precipitation when mixing two or more polymers.

The use of chloroform also allows one to make all the possible mathematical combinations by mixing all of the above blends i.e., one could make a blend of PPQ/cellulose acetate/and polyvinylpyrrolidone, etc. This combination of three or more polymers or other possible combinations will be the subject of a further study for making polymeric membranes.

SUMMARY

Compatibilization of PPQ polymer with other polymers such as polyvinylacetate (low, medium and high molecular weight), polyvinylpyrrolidone, vinylpyrrolidone/vinyl acetate copolymer, polybrene, cellulose acetate and cellulose triacetate was accomplished by using chloroform as the solvent medium. The above solution blends are used to prepare polymeric membranes that may be useful as battery separators.

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