

Chemical Modification of Acrylonitrile Copolymers: Reaction of Cationic Copolymers with Ethylene Oxide

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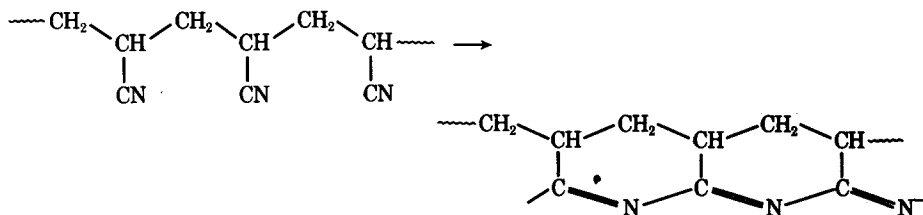
Synopsis

Copolymers of tertiary amines have been reacted with ethylene oxide gas. The reaction induces low temperature cyclization and increases polymer hydrophilicity. When the copolymer is in film form, water permeability is dependent on ethylene oxide processing time and temperature.

The behavior of the copolymer films when treated with ethylene oxide is contrasted with the effects due to thermal treatment of acrylonitrile copolymers.

INTRODUCTION

The results of thermally treating acrylonitrile (AN) and its copolymers have been widely reported.¹⁻⁷ In particular, Grassie^{2,7} has attributed the discoloration resulting from treatment at 100–200°C to nitrile group polymerization leading to tetrahyronaphthyridine rings:



The formation of C=N conjugation is confirmed by an increase in infrared absorption at 1590 cm^{-1} . It has also been shown that the initiation of the ladder structure is enhanced by electrophilic groups and that copolymers of AN are preferable to polyacrylonitrile (PAN) itself.

The incorporation of a stable ladder structure into membranes might prove beneficial by increasing solvent resistance and thus extending the possible range of membrane applications. Such a material should preferably be produced under conditions less rigorous than those used in the thermal treatment of PAN. In addition, if the membranes are to be used for applications such as ultrafiltration, reverse osmosis, or dialysis, a degree of hydrophilicity is essential. The investigation described here was designed to produce and evaluate hydrophilic ladder polymers.

The method chosen was to react AN copolymers with ethylene oxide gas. Ethylene oxide has previously been reacted with poly(vinyl alcohol)⁸ and polyamides⁹ under the conditions of elevated temperature and pressure. Graft copolymerization may be achieved by reacting polyamide, polyureas, or polyurethanes with liquid ethylene oxide under pressure.¹⁰ However, AN copolymers can be chemically modified by ethylene oxide without the necessity of high pressure or temperature.¹¹ The suitability of the technique has been evaluated by considering the effect of treatment with ethylene oxide on a copolymer of AN with the tertiary amine dimethylaminoethyl methacrylate (DMAEMA). The influence of ethylene oxide on the ultrafiltration properties of the copolymer have been studied.

EXPERIMENTAL

Polymer Preparation. AN was supplied by British Drug Houses Ltd. and DMAEMA, by Rohm and Haas (U.K.) Ltd. The copolymer was produced by free-radical redox polymerization from a monomer weight ratio AN:DMAEMA of 85:15.

Film Formation. Polymers were produced in film form by solvent casting from solutions in dimethylformamide (DMF). The casting substrate was glass and the solution concentration 10% w/v.

Chemical Modification. The modification of membranes by treatment with ethylene oxide is carried out by an adaptation of a clinical procedure for ethylene oxide sterilization.¹¹ This procedure involves contacting the films with pure ethylene oxide gas at a slightly reduced pressure and at a concentration in excess of 1400 mg/l.

Ultrafiltration Measurement. Values for membrane water permeability were obtained from an ultrafiltration cell containing a stainless steel disc as membrane support.¹²

Infrared Spectroscopy. The infrared spectra of films were obtained by using a Perkin-Elmer 125 spectrometer.

DISCUSSION

Films samples of AN-DMAEMA were treated with ethylene oxide for a range of times at 30° and 60°C. Values for water permeability are given in Table I.

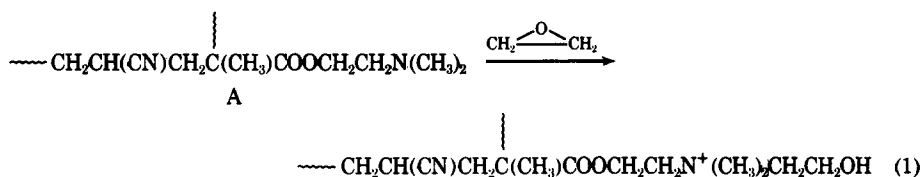
The principal features arising from modification are as follows: (1) Modified films are yellow in colour and insoluble in DMF. (2) Modification brings about a rapid increase in hydrophilicity followed by a gradual decrease. (3) Water permeability is dependent on modification processing time and temperature. (4) Comparison of the infrared spectra of modified and unmodified films indicates that modification results in the development of peaks at 3300 cm^{-1} and 1590 cm^{-1} .

Reaction between ethylene oxide gas and AN-DMAEMA copolymer leads to changes in copolymer color, solubility, and film properties. This is believed to involve ring opening and the breaking of the highly polar carbon-oxygen bond. By analogy with the reaction between epoxide resins and tertiary amines.^{13,14}

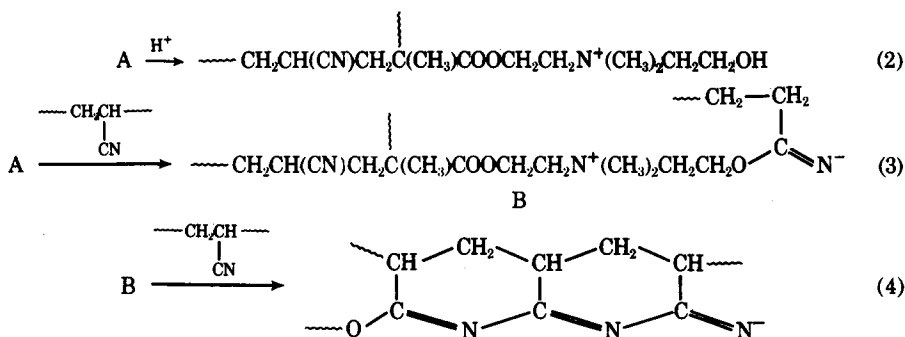
TABLE I

Temperature, °C	Processing time, hr	Water permeability, ml min ⁻¹ cm ⁻² torr ⁻¹ 10 ⁶
—	0	0
30	2	3.79
	4	9.00
	8	6.63
	16	5.86
60	1	3.84
	3	6.28
	5	3.85
	8	3.41
	16	1.76

reaction of AN–DMAEMA copolymer with ethylene oxide should be expected to proceed as follows:



This intermediate compound A could readily undergo further reactions:



Reaction (2) would account for the infrared absorption OH peak at 3300 cm⁻¹ and the increase in hydrophilicity. Reactions (3) and (4), on the basis of evidence from the thermal degradation of PAN,^{1,2} would account for the development of color, insolubility, and the presence of an infrared absorption peak at 1590 cm⁻¹. Competition between reaction (2) and reactions (3) and (4) would explain the dependence of film properties on processing temperatures and processing time.

The chemical modification of AN copolymer films appears to justify further study. The ladder structure of the modified films may extend the range of membrane separation processes in comparison with that of conventional cellulose and cellulose acetate films. Of particular interest is the extent to which membrane properties can be controlled by chemical modification and if the degree of control will permit the design of membranes with distinctive solute molecular weight cut-offs.

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Received August 8, 1974

Revised October 30, 1974