NEW THERMALLY STABLE ADHESIVE RESINS

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(including experimental work by J. VERBORGT, I. HADDAD, S. HURLEY and P. SIVARAMAKRISHNAN)

ABSTRACT

Two new classes of adhesive resins with good thermal stability have been prepared. One class comprises units of aromatic ether, ketone and sulphone with nitrile side groups and the other class, units of m/p-arylene sulphides with nitrile side groups. Both classes are relatively low melting and when melted will wet surfaces of glass, metal and carbon fibres and give good bonds. They can be crosslinked without gas formation on heating alone or with catalysts but the crosslinked materials became rubbery at about 200–250 °C. They are stable in circulating air at 300 °C for about 200 hours.

There is a need for thermally stable adhesive resins which have long life at elevated temperatures even in air. In general, what is needed is a linear polymer with good solubility in common organic solvents which does not melt much above 200 °C. It should flow readily above its melting point and on wet surfaces such as metals, glass, carbon fibres, etc. in order to give good adhesion. Then it should be possible by heating to convert the resin into a crosslinked structure without liberation of any volatile byproducts and still maintain good adhesion and strength.

At present the best resins for adhesion and binding of composites are probably the epoxy resins. These have excellent adhesive characteristics and are moderately strong but they do not hold up in strength above about 200 °C and the present need is for higher surface temperatures. Also the epoxy resins have to be compounded as they are used and it would be helpful if this could be avoided.

For some time we have been searching for polymers which will have these desirable properties. Two classes of backbone polymers which approach these requirements have been prepared and are currently under study in our laboratories. The problem still before us is the last crosslinking step and that has only been partially solved.

A number of polymers made from diphenyl ether and its *p,p'*-disulphonyl chloride have been described and these are good high-temperature plastics[1]. Those thus far produced are high melting and not very soluble so they do not fit the specifications which we have been asked to meet. Also polymeric ketones have been made from iso- and tere-phthaloyl chlorides and diphenyl

ether[2] and these are high melting and difficult to fabricate and they do not meet our needs.

By combining these units we have made one of our promising polymers which has a backbone made up of units of aromatic ethers, aromatic sulphones and aromatic ketones. It is readily prepared by a Friedel–Crafts reaction at room temperature and can be obtained in the viscosity range of 0.75–0.9 quite readily. It can be produced in the right melting range and it is quite stable to heat and oxidation. In addition to the units mentioned above a polymer has been made with nitrile groups pendant to the chain or at the ends. It was hoped these nitrile groups could be trimerized by heat and catalysts to give the stable type of crosslink needed without void formation and hence meet our requirements.

It is relatively easy to convert aryl nitriles into aryltriazines:
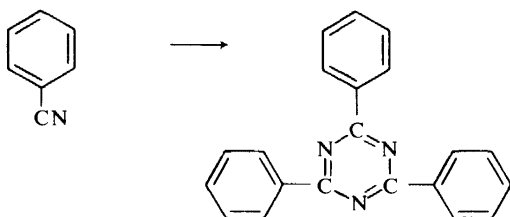

The most promising of this class of polymer has been made by condensing diphenyl ether and m-benzenedisulphonyl chloride, using ferric chloride as catalyst, to give one monomer needed in the final synthesis.
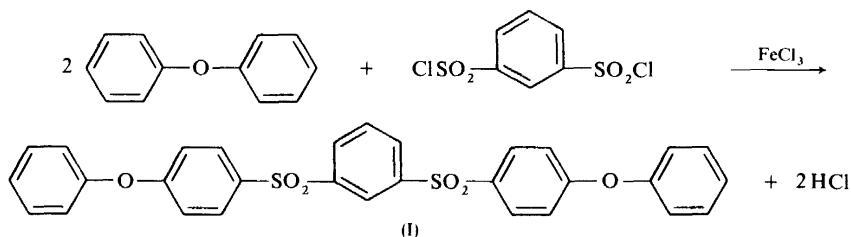
This unit was then used as one monomer and the other monomer was isophthaloyl chloride or a mixture of iso- and tere-phthaloyl chlorides with some 5-cyanoisophthaloyl chloride. Sometimes another monomer was prepared from 5-cyanoisophthaloyl chloride and diphenyl ether and this was used along with the sulphonyl ether and isophthaloyl chloride to give the principle polymer.

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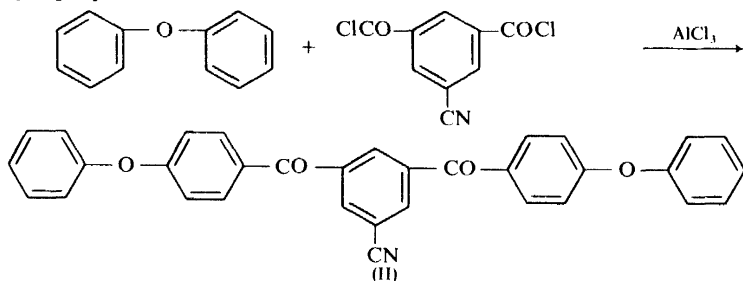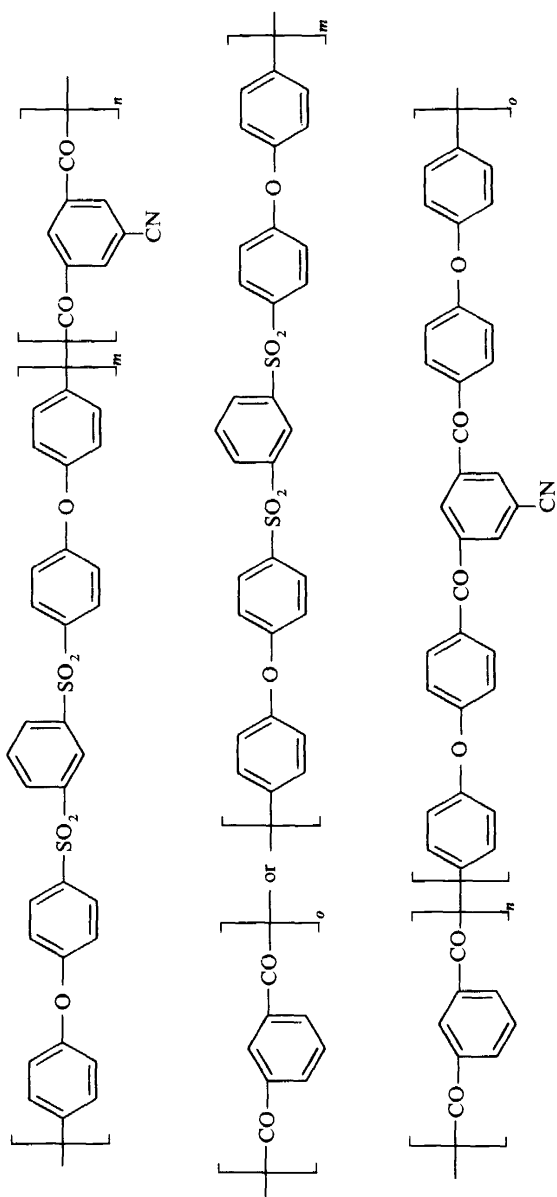
(III)

In the preparation of the final polymer, aluminium chloride was used as catalyst and 1,2-dichloroethane was used as solvent, to condense monomers (I) and (II) (and sometimes extra isophthaloyl chloride and/or terephthaloyl chloride) to give polymers with a backbone having a variety of units which results in good solubility and moderate melting temperatures. Reaction was at room temperature for varying lengths of time and the longer runs gave higher viscosity polymers. As the reaction proceeded polymer precipitated from the solvent but apparently continued to grow in size.

There is no evidence that the solvent is incorporated into the polymer since neither analysis nor infra-red spectral examination of the product indicates its presence in the polymer. Yet is is important for this reaction mixture since other solvents have proved less effective.

At the end of the reaction time the polymer was collected on a filter and washed thoroughly with water and methanol to remove essentially all of the catalyst. The yield was essentially quantitative and the melting point varied from about 190–215 °C depending on the monomers used in the reaction.

The first polymer has a composition indicated by structure (III). Sometimes there are terephthaloyl groups used in the connecting steps as well as isophthaloyl groups.

These various polymers were soluble in NN-dimethylacetamide. When they were heated at 230–250 °C for 20–24 h they became insoluble. However, they were all lightly crosslinked and would become soft and rubbery at about 250–300 °C. The uncrosslinked polymer showed a break in a thermogravimetric analysis test at 550 °C in air but it lost one to three per cent of its weight when heated for 200 h at 300 °C in air. At 350 °C the weight loss was six to ten per cent and at 375 °C about 75 per cent.

It was hoped that the crosslinked material would be formed by trimerization of the pendant nitrile groups to give triazine units (IV).


(IV)
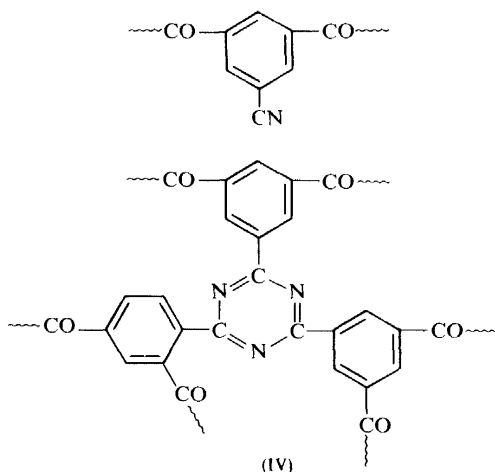
The uncrosslinked polymers adhered strongly to metals such as aluminium

and titanium, to glass fibres and to carbon fibres. They gave excellent laminates when pressed on to glass cloth. Tests indicated they were superior to epoxies in strength of the laminates and intermetal bonds. However, the crosslinked specimen did not stand up to oxidation as well as did the uncrosslinked variety and hence there is some question as to just how crosslinking had actually occurred. The nitrile absorption in the infra-red region shown by the uncrosslinked material disappeared on heating of the specimen but it is impossible to check for triazine formation since that unit absorbs where the aromatic rings absorb in the infra-red spectrum and hence would not be distinguishable if were present.

These polymers have been described[3] and more data will be avilable as more work is done.

Another interesting group of polymers has been made by condensing aromatic dibromides with m-benzenedithiol in NN-dimethylformamide or NN-dimethylacetamide, potassium carbonate being used to absorb the hydrogen halide liberated. After studying a number of model compounds it was decided that the best combination of reagents was m-benzenedithiol and p-dibromobenzene to give a polymer with mixed *meta* and *para* linkages.
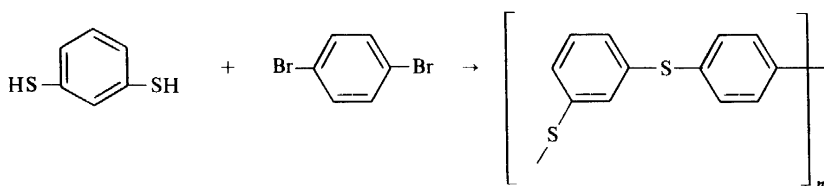

A number of polyarylene sulphides have been described[4]. These are in general *para* linked units, high melting and slightly soluble. The use of mixed *para* and *meta* linked groups gave better melting points for our needs and also greater solubility in common organic solvents[5].

This *meta–para*-polymer could be obtained wlth an inherent viscosity of about 0.4 and it was soluble in hexamethylphosphoramide. By replacing a part of the p-dibromobenzene with either 2,4-dichlorobenzonitrile or 3,5-dichlorobenzonitrile copolymers were obtained with pendant nitrile groups.
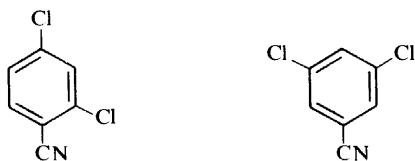
The molecular weights indicated by inherent viscosity were slightly lower than in the case where no nitrile groups were present. The melting points of the polymer were somewhat lower in this series of polymers than in the oxo-ether sulphones. The polymer without nitrile substitution melted at 100–135 °C and those with nitrile side groups melted about 20° lower.
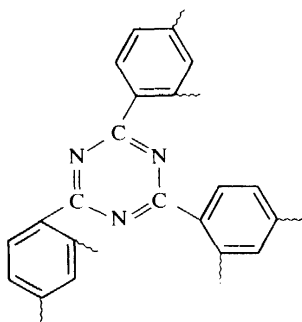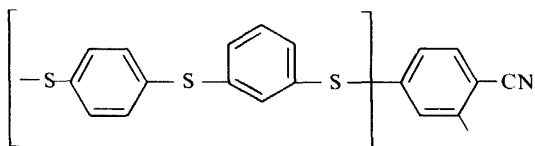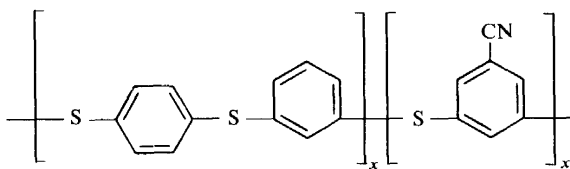
The polymers containing nitrile groups could be crosslinked by heating them with small amounts of zinc chloride at about 290 °C or at 350–400 °C without a catalyst. All of the crosslinked polymers in this series were very little less stable in air than the uncrosslinked variety. When the zinc chloride catalyst was removed by water extraction before isothermal ageing, tests show these crosslinked polymers were about as stable as the uncrosslinked polymers.

One uncrosslinked sample lost 2.4 per cent of its weight in ten days at 300 °C and the same material after crosslinking lost 2.3 per cent of its weight in the same time. Another sample lost 2.9 per cent of its weight at 300 °C in ten days and after crosslinking it lost only 1.5 per cent of its weight under same conditions. The crosslinking reaction was somewhat erratic and not all samples became insoluble when heated. All samples showed strong adhesion to glass fabrics and gave good looking laminates. These polymers were also very adhesive to metal surfaces. The crosslinked samples all seemed to be more or less rubbery in these cases too. Details of the synthesis and properties of the various polymers prepared will be fully described in other publications[5].

It seems probable from our work up to now that we have insufficient crosslink density in any of our samples to give rigid materials. We did not seem to improve this situation by increasing the amount of nitrile side groups introduced into these molecules. Hence, it may be that in such rigid linear

chains that it is not possible to get three nitrile groups in proper position to give triazine links to any appreciable extent. The final answer is not yet available to us. We have plans to make some polymers with longer side chains to give greater mobility to the molecules to see if we can avoid our present difficulties.

ACKNOWLEDGEMENT

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