

Copper catalysed gelation of dilute poly(acrylonitrile) solutions

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Metallic copper catalysed gelation of dilute poly(acrylonitrile) solutions in dimethylformamide was discovered and studied by infra-red spectroscopy and other techniques for the first time. It was observed that some cyano groups were converted to carboxyl groups. Gelation did not lead to any increase in molecular weight. An intermolecular hydrogen bonding model is proposed to explain the behaviour of the gelated polymer. The gelation mechanism is given on the basis that metallic copper has a catalytic effect on the hydration of nitriles and that the partially neutralized acid component tightly coils the chain to cause the precipitation of poly(acrylonitrile).

(Keywords: poly(acrylonitrile); copper; gelation; catalysis)

INTRODUCTION

Poly(acrylonitrile) (PAN) exhibits various kinds of gelation phenomena in many solvents which are undesirable in the fibre industry. The reversible gelation of concentrated PAN solutions in *N,N*-dimethylformamide (DMF) is ascribed to the formation of a three-dimensional network and the crosslinks are assumed to be crystalline nuclei in the supersaturated solutions^{1,2}. Another commonly known irreversible gelation takes place at high temperatures with evolution of HCN, which leaves double bonds in the macromolecules to react with each other and form a three-dimensional network. This paper presents the results of our recent studies on the metallic copper catalysed gelation of dilute PAN solutions. We discovered this phenomenon when we were investigating the interfacial behaviour of polymer-metal composites. It is shown that this type of gelation is due mainly to the formation of hydrogen bond crosslinks and the restraint of the conformation of polymer chains in DMF.

EXPERIMENTAL

All reagents were commercially available from Shanghai Chemical Co. and were of chemically pure grade. The electrolytically refined copper sheets were $10 \times 10 \times 0.1 \text{ mm}^3$.

After removal of the polymerization inhibitor by distillation under reduced pressure, 22 g of acrylonitrile, initiated by potassium persulphate (0.10 g), were polymerized in a water slurry at 50°C ³. The polymer (20 g) was carefully washed with methanol and dried *in vacuo* at 60°C overnight. The solvent DMF (500 ml) was dried over P_2O_5 (10 g for the first day and 5 g of fresh oxide for each additional day) for 3 days, filtered off, neutralized with 20 g KOH pellets and distilled under reduced pressure. The water content in the solvent thus pretreated was claimed⁴ to be as low as $4 \times 10^{-3} \text{ M}$.

The chemically cleaned copper sheets (2.0 g) were prepared by etching with dilute HNO_3 , rinsing with water

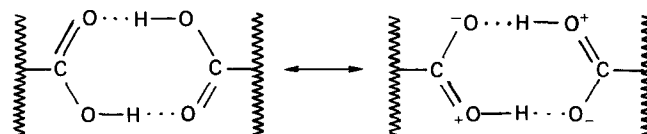
and ethanol repeatedly just before they were immersed in a PAN solution (0.30 g PAN dissolved in 30 ml DMF). Stirring at ambient temperature ($15\text{--}20^\circ\text{C}$) for 1 day turned the polymer solution green. After continuous agitation for 2 days, the reaction beaker was allowed to rest for 3 days, yielding a green gel which was washed with methanol several times and dried *in vacuo* at room temperature to constant weight (0.30 g).

The gel could also be obtained by using copper powder.

Infra-red (i.r.) spectra were recorded on a Nicolet 170sx Fourier transform spectrometer. X-ray photoelectron spectra were obtained on a VG Scientific Escalab (mark 2), using a residual pump oil contamination line as the internal standard. Molecular weights were measured using a Ubbelohde viscosimeter at 25°C , according to the relation⁵: $[\eta] = 1.66 \times 10^{-2} \text{ M}^{0.81}$. Differential scanning calorimetry (d.s.c.) scans were acquired with a Perkin-Elmer DSC-2C differential scanning calorimeter, using a scanning rate of $20^\circ\text{C min}^{-1}$.

RESULTS

The i.r. spectrum of the dry gel shows that some nitrile groups are converted to carboxyl groups (Figure 1B). The new medium absorption bands at 1737 and 1175 cm^{-1} correspond to the $\text{C}=\text{O}$ and $\text{C}-\text{O}$ stretching vibration modes, respectively⁶. The broad weak band near 922 cm^{-1} is fairly good evidence for the existence of dimeric carboxylic acid and often attributed to the out-of-plane $\text{O}-\text{H}\cdots\text{O}$ deformation with the following structure⁶:



Scheme 1

The band at 1585 cm^{-1} , with intensity varying from weak to medium, is assigned to the stretching of carboxyl

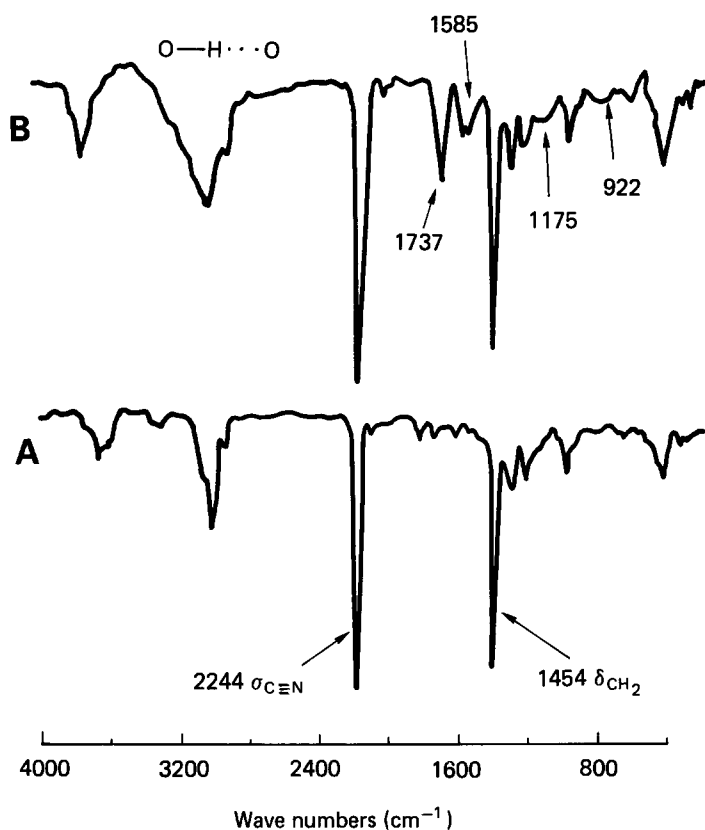


Figure 1 I.r. spectrum of (A) PAN and (B) dry PAN gel

Table 1 Viscosity-average molecular weight ($\times 10^4$) of PAN

	Before gelation	After gelation
Sample 1	10.6	8.4
Sample 2	9.0	8.0

groups in salt form⁶ since this band almost disappears when the green gel is decoloured by the addition of a few drops of HCl or H₃PO₄. The X-ray photoelectron spectroscopy studies of the dried gel indicate that copper exists in the gel as the Cu²⁺ ion as in the reacted copper sheet surface.

The molecular weight measurements of PAN before and after gelation show a slight decrease in the viscosity-average molecular weight (\bar{M}_v , Table 1). Since DMF molecules are strongly bonded both to acrylic acid segments through hydrogen bonding and to Cu²⁺ ions through coordination bonding, which make it very difficult to exclude them from the gel, the slight decrease in \bar{M}_v is attributed to the solvent residues in the dry gel.

Although the intensity of the carboxyl vibration is relatively weak compared with that of C≡N stretching, a couple of carboxyl groups beside a polymer chain is sufficient to restrain the conformation of the macromolecules in the solvent. It is unlikely that primary valent crosslinks exist between the chains. Nonetheless, the carboxyl groups from one polymer molecule will be capable of reacting with those of another polymer molecule to form intermolecular hydrogen bonds (Scheme 1). Considering this point, the best model proposed to describe the gelled PAN structure may be a hydrogen-bonded version characteristic of partial neutralization of

the acrylic acid segments by Cu²⁺ ions within a polymer chain. This model can be employed to explain many properties of gelled PAN besides the result from molecular measurements:

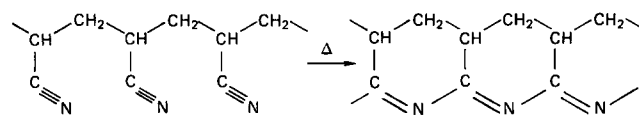
1. The gel cannot be destroyed by acids such as HCl and H₃PO₄ although decolouration occurs. If the gel was mainly crosslinked by copper(II) acrylate, the gel would show fluidity in acidic solutions. However, the intermolecular hydrogen bonds cause insolubility.
2. Pouring large amounts of DMF into the gel or heating the gel will redissolve it. This indicates that intermolecular crosslinks in a covalent-bonded form do not exist in the gel. Cooling the heated gel solution to room temperature leads to gelation again, which is evidence that coiling of the chains plays an important role in the molecular motion during gelation.
3. Prolonged heating of the gel solution will turn it yellow or heating the dry gel at 200°C will turn it into a black solid. The implications here are that the colour change is due to a conjugated structure as proposed by Grassie *et al.*⁷ (Schemes 2 and 3).

D.s.c. studies of the dry gel indicate that its glass transition temperature has been raised from 386 to 405 K whereas the cyclization temperature has been decreased from 576 to 542 K (Figure 2) due to the catalytic effect of the neighbouring acrylic acid component.

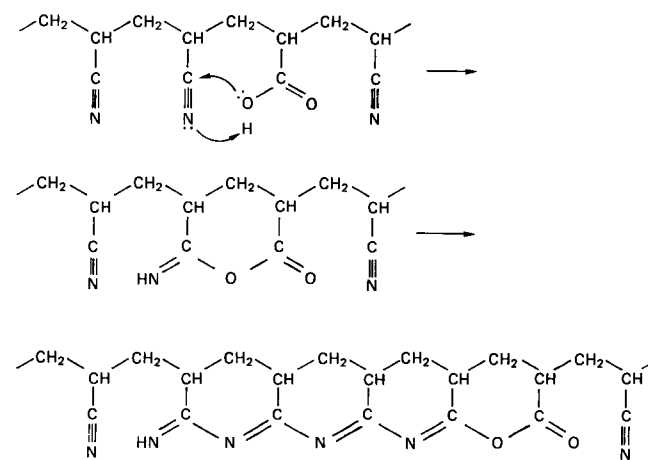
DISCUSSION

Catalytic effect of copper(0)

Sugiyama *et al.* have studied the adsorption state of acrylonitrile on copper(0) surfaces⁸. According to their molecular orbital CNDO calculations, when the cyano group is side-on coordinated to surface copper atoms to reduce the carbon–nitrogen bond order to 2.5, the surface adsorbate–adsorbent system gains less energy than in any other end-on adsorption state (Scheme 4). Fourier



Scheme 2



Scheme 3

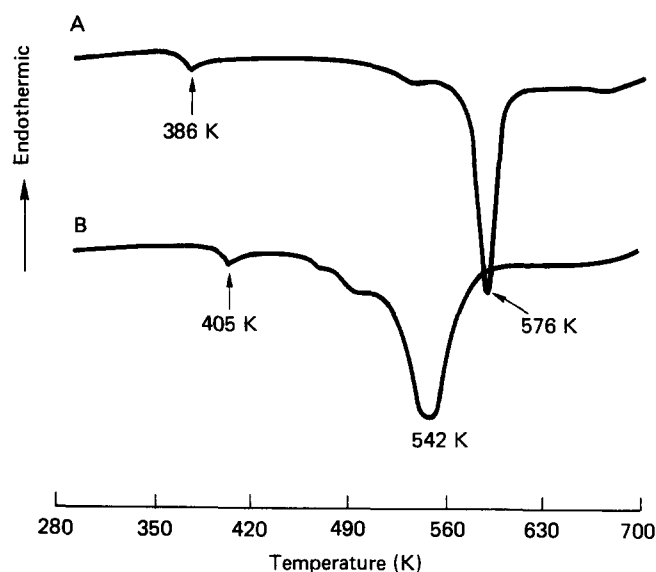


Figure 2 D.s.c. curves of (A) PAN and (B) dry PAN gel



Scheme 4

transform infra-red spectroscopic studies of acrylonitrile adsorbed on a silica-supported copper(0) catalyst directly reveal the existence of a side-on interaction between the cyano group and the copper(0) surface site⁹. This is regarded as the main cause for the facile hydration of the cyano group to amide on copper(0) catalyst⁸⁻¹¹. In our experiment, water cannot be completely expelled during gelation. However, when the reaction was not brought into contact with atmospheric moisture, gelation was greatly delayed. It was also found that PAN prepared from other solutions such as DMF and tetrahydrofuran could lead to gelation under atmospheric conditions. Therefore it is likely that PAN undergoes a successive hydration from the cyano group, via amide to the carboxyl group in the presence of metallic copper and atmospheric moisture alike. Since PAN prepared by conventional peroxide initiators cannot be hydrolysed¹² by steam even at 150°C and 513 MPa, we believe that the gelation is catalysed by copper metal. In contrast, zinc and iron powder were found to be unable to catalyse a similar gelation.

I.r. studies confirm the above conjecture. When anhydrous alcohol (5 ml) was added to the reacted solution (1 ml) to precipitate the intermediate species before gelation occurred, the characteristic amide I (1666 cm⁻¹) and amide II (1628 cm⁻¹) absorption bands¹³ could be observed in the i.r. spectrum of the precipitated PAN, as well as the 1737 cm⁻¹ band attributed to the acrylic acid component (Figure 3A). When water was added to the polymer solution before reaction, an acrylonitrile-acrylamide copolymer was formed which was precipitated from solution, thereby preventing the acrylamide component from further

hydration to acrylic acid. The copolymer has no i.r. band at 1737 cm⁻¹ (Figure 3B). No report on the hydration of amide to carboxylic acid on metal surfaces has been made previously. The gelation of PAN which begins with nitrile groups is obviously featured by the packed distribution of a large amount of polar cyano groups beside the chain.

Comparison with nucleation gelation

It was previously observed that a very dilute PAN solution (0.14 wt%) in DMF/copper(0) also formed a gel after standing in the atmosphere for 30 days. In the meantime, the original dilute PAN solution in which no copper sheet had been immersed showed no observable phenomenon. On the other hand, Bisschops's reversible nucleation gelation of PAN solutions occurs at concentrations varying from 18 to 23 wt% even at -10°C^{1,2}. Such concentrated solutions actually belong to thermally unstable supersaturated solutions, whereas the copper catalysed gelation is a chemical process. It is noticeable that the latter may be accelerated by nucleation if the copper-treated PAN solution is concentrated to ~20 wt% by removing the solvent under reduced pressure.

Poly(acrylic acid) is soluble in DMF. When the two neighbouring acid groups are neutralized with Cu²⁺ ions, the segments of poly(acrylic acid) are tightly coiled, reducing the solubility of PAN as Cu²⁺ ions continuously enter the solution. Gelation or precipitation is often observed in the salting-out process of polyelectrolytes¹⁴. In our case, an equilibrium is obtained at the 'gel point' when the precipitating effect of copper(II) acrylate segments and the interaction of hydrogen bonds between two chains outweigh the dissolution tendency of

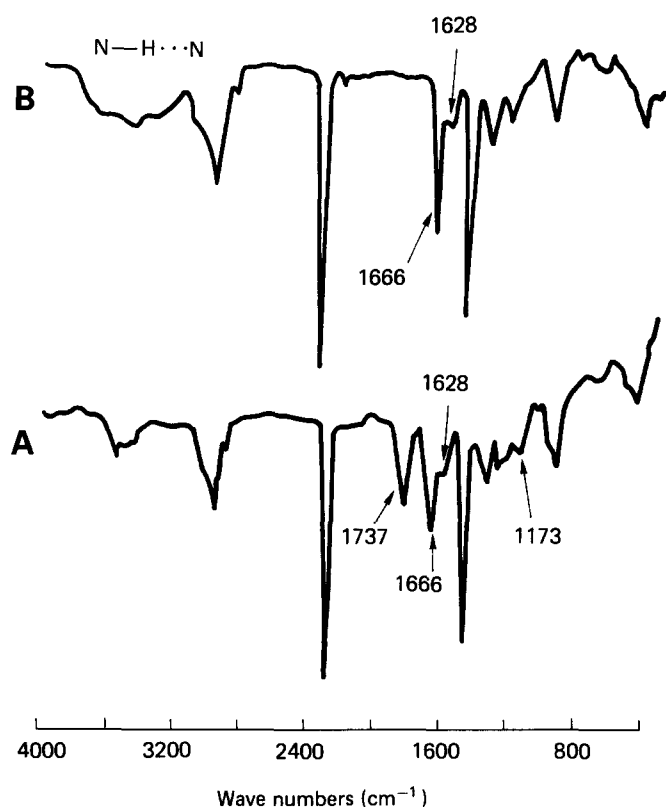


Figure 3 I.r. spectrum of precipitated PAN obtained by (A) adding anhydrous alcohol to the reacted solution just before gelation and (B) adding water to the PAN solution before reaction

acrylonitrile and acrylic acid segments. The polymer solution loses fluidity when sufficient hydrogen bond crosslinks and intramolecular chemical bonds severely restrain the conformations of PAN chains in DMF.

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REFERENCES

- 1 Bisschops, J. *J. Polym. Sci.* 1954, **12**, 583
- 2 Bisschops, J. *J. Polym. Sci.* 1955, **17**, 89
- 3 Sorenson, W. R. and Campbell, T. W. 'Preparative Methods of Polymer Chemistry', Interscience Publishers, New York, 1961, Ch. 4
- 4 Riddick, J. and Bunger, W. 'Techniques of Chemistry, Vol. 2: Organic Solvents', 3rd Edn, Wiley-Interscience, New York, 1970, p. 838
- 5 Bisschops, J. *J. Polym. Sci.* 1955, **17**, 81
- 6 Socrates, G. 'Infrared Characteristic Group Frequencies', John Wiley & Sons, Chichester, 1980, pp. 64-66
- 7 Fettes, E. N. 'Chemical Reactions of Polymers', Interscience Publishers, New York, 1964, pp. 613-626
- 8 Sugiyama, K., Hiroshi, M. and Tsuneo, M. *Hyomen* 1987, **25**, 666
- 9 Sugiyama, K., Hiroshi, M., Sokiwa, H. and Matzuda, F. *Chem. Lett.* 1986, 2093
- 10 Ravindranathan, M., Kalyanam, N. and Sivaram, S. *J. Org. Chem.* 1982, **47**, 4812
- 11 Matzuda, F. *Chemtech.* 1977, 308
- 12 Prince, M. and Hornyak, J. *J. Polym. Sci. A1* 1967, **5**, 161
- 13 Socrates, G. 'Infrared Characteristic Group Frequencies', John Wiley & Sons, Chichester, 1980, p. 74
- 14 Armstrong, R. W. in 'Encyclopaedia of Polymer Science and Technology' (Eds H. Mark, N. Gaylard and N. Bikales), Vol. 10, Interscience Publishers, New York, 1969, p. 827