

Degradation of polyacrylonitrile in solution by alkali

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This paper presents new data about changes which occur in viscosity, number-average molecular weight and the Huggins constant when polyacrylonitrile is degraded by alkali. The significance of these changes in relation to chain scission reactions, structural alteration and hydrolysis processes inherent in the overall degradation is considered in some detail. Tentative explanations for the apparent recovery in viscosity and molecular weight characteristics on extended exposure to dilute alkali are put forward.

INTRODUCTION

The thermal¹⁻⁶ and alkali⁷⁻⁹ induced degradation of polyacrylonitrile has received considerable attention in the past with the greater emphasis being placed on the former approach. Aspects such as possible chain scission mechanisms, thermal stability and the generation of colour have all aroused interest. Several possible structural changes, ensuing from degradation, have been considered in the literature⁹⁻²⁵ so they will not be repeated here. Our interest is in changes which take place in the polymer structure and also in colouration during the reaction of polyacrylonitrile with alkali. The former have been examined through molecular weight dependent properties and variations in polymer crystallinity while the latter point was investigated using computer analysis of colour-constitution relationships. Here we report observations related to main chain cleavage arising from alkali induced degradation of polyacrylonitrile.

EXPERIMENTAL

Polyacrylonitrile was prepared in solution by γ irradiation of acrylonitrile in dimethylformamide under high vacuum (1.33×10^{-2} N/m²) using sealed ampoules. The monomer solution (0.33 mol acrylonitrile: 0.67 mol DMF), was irradiated at 4 rad/sec for 8.6×10^4 sec. About 60% of the monomer was polymerized. The resulting polymer solution was diluted to 10 times its volume with DMF and stirred to provide a clear, mobile solution. Precipitation of the polymer, by pouring the solution into 10 times its volume of rapidly stirred water, was followed by filtration (porosity 4 sintered crucible). The resulting polymer was thoroughly washed with water and methanol before drying to constant weight under vacuum at 313K.

Samples of polymer solution were prepared by dissolving tared amounts in dimethylformamide to give 17.4 g/dm³. The density at 293K was measured as 0.9518 kg/dm³.

75 cm³ aliquots of the above solution were measured

into sealed flasks and the whole warmed to 303K in a water bath. The samples were rapidly stirred using a magnetic stirrer while 0.50 cm³ of potassium hydroxide solution (in water) was added. The stopper was immediately replaced and the flask returned to the water bath. A stopwatch was started during the addition of alkali. The alkali concentration was varied in the range 0.8 to 18% w/v, corresponding to 5.3×10^{-2} to 1.2 g KOH/dm³ of polymer solution.

Samples were removed by pipette at times ranging from 300 to 6×10^5 sec after the addition of alkali. The polymer was precipitated by running the solution from the pipette into an excess of methanol or methanol-ether. Methanol was suitable for precipitating the less highly coloured samples. After more extensive reaction, however, methanol was less satisfactory since part of the colour remained in solution, indicating possible fractionation. It was found that less polar methanol/diethyl ether mixtures gave more effective precipitation. The optimum ether content varied from 0-10% for lightly coloured samples to about 50% for strongly coloured samples. The polymer was filtered on porosity 4 sintered glass crucibles, washed with the mixed solvent and dried under vacuum at 313K.

An Ubbelohde suspended level dilution viscometer was used for viscometry carried out using dimethylformamide as the solvent. Measurements of flow times were taken at 303K for samples of polyacrylonitrile, degraded to different extents as described above. Precautions were taken to avoid adsorption of water by the solvent and solutions. Number-average molecular weights were estimated using a Hewlett-Packard Model 501 high speed osmometer. Hydroxyethyl cellulose membranes were used²⁶. DMF was used as the solvent and solutions were protected against moisture adsorption. Osmometry was carried out at 310K. π/c values were plotted against the concentration (c) and extrapolated by the least mean squares procedure to $c = 0$. Treatment of viscometric data was limited to calculation of intrinsic viscosities. This is considered to be the most realistic way of presenting the information owing to the changes in the polymer, incurred as a consequence of degradation treatment. Hence, calculation of the corresponding viscosity-average molecular weights is not possible, owing to the absence of Mark-Houwink parameters.

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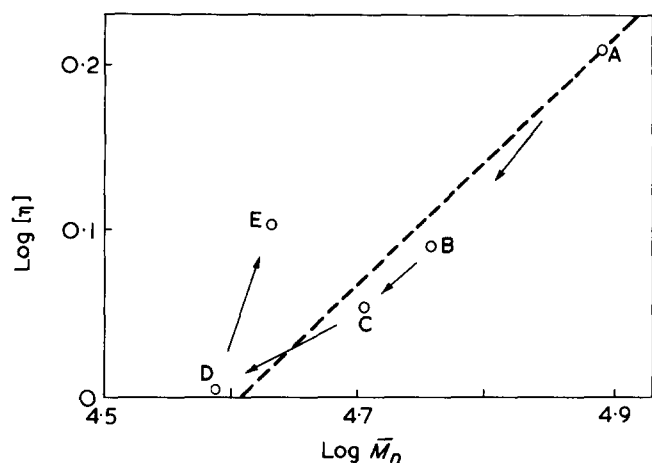


Figure 1 Log-log plot of the variation in intrinsic viscosity with \bar{M}_n for samples of different degradation treatments: A, no alkali; B, 6×10^2 sec; C, 1.18×10^3 sec; D, 4×10^3 sec and E, 9×10^3 sec degradation with 0.1 g KOH/dm^3 of polymer solution

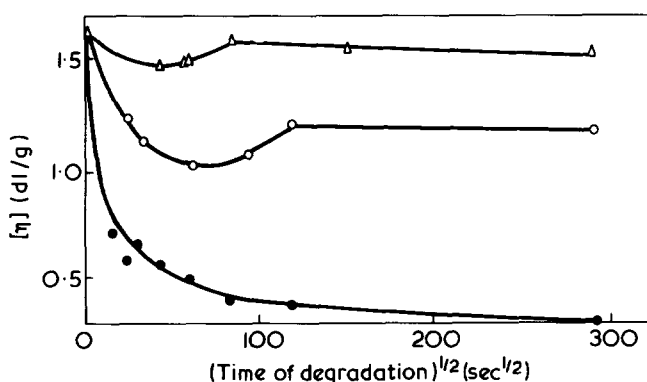


Figure 2 Change in the intrinsic viscosity with $(\text{time})^{1/2}$, for various concentrations of added KOH solution. Δ , 0.05 g/dm^3 ; \circ , 0.10 g/dm^3 ; \bullet , 0.50 g/dm^3

RESULTS

Figure 1 shows the intrinsic viscosity, $[\eta]$, plotted on a log-log basis against the number-average molecular weight, \bar{M}_n , for polyacrylonitrile treated with the specified alkali concentration at the quoted times. In the absence of complicating factors, a homopolymer in solution should give a linear plot of slope α (usually quoted at 0.75 for polyacrylonitrile in dimethyl formamide at 303K). Point A relates to undegraded polyacrylonitrile in dimethylformamide. Points B and C are slightly lower in $[\eta]$ than would be expected for polyacrylonitrile which was undegraded but of the corresponding number-average molecular weight. In contrast points D and E are higher in $[\eta]$. Point E shows an increase both in viscosity and molecular weight. Thus the number-average molecular weight, \bar{M}_n , falls during alkaline treatment but increasing exposure produces a significant level of apparent recovery.

In Figure 2, $[\eta]$ is plotted against $t^{1/2}$, where t denotes the time of reaction at various alkali concentrations. At all concentrations there is initially a drop in $[\eta]$. This is followed by a measurable increase in $[\eta]$, the extent of recovery being greater at lower alkali concentrations. $[\eta]$

apparently decreases slowly after this recovery. In Figure 3, we have the change in the value of k' from the Huggins equation when plotted against $t^{1/2}$, the time of reaction being t , as previously. Though the uncertainty in k' is quite large, the data clearly show that k' increases at first before undergoing a gradual decrease. The rate of such decreases is strongly dependent on the concentration of alkali used.

As an extension of viscometric studies, a comparison was made between an undegraded polyacrylonitrile sample and one of the more highly degraded samples (0.5 g KOH/dm^3 for 1.6×10^5 sec). The intrinsic viscosities and Huggins constants were obtained for solutions of both polymers for a series of dimethylformamide-acetic acid mixed solvent compositions. For this work the polymer was dissolved in dimethylformamide and the acetic acid carefully added to give the required composition of mixed solvent. Dilutions during viscometry were made using mixed solvents of identical composition as that used to make up each individual solution. The results are given in Figure 4. All measurements were carried out at 303K. The undegraded polymer was precipitated by the addition of 12% (w/w) acetic acid to the dimethylformamide, whilst an addition of 33% (w/w) was required to cause precipitation of the degraded polymer sample. Corresponding viscometric studies show a sudden drop in $[\eta]$ at 11% (w/w) and 26% (w/w) of acetic acid in dimethylformamide, respectively. These ratios of acetic acid in dimethylformamide can be considered to be θ solvents for the undegraded and degraded polymer samples, respectively, at the quoted temperature. Figure 5 demonstrates the sensitivity of the Huggins' constant of these same polymer-mixed solvent compositions to the concentration of acetic acid in the mixed solvent.

DISCUSSION

The reduction in $[\eta]$, observed in the initial stages of treatment of polyacrylonitrile with alkali, must arise mainly from a drop in the average molecular size of the chains. This conclusion is supported by the results of the osmometry studies and the behaviour has been noted by McCartney⁹. It can be seen from Figure 1 that the viscosity of treated sample becomes successively lower, and then higher than that of unreacted polyacrylonitrile of the same molecular weight.

The initial lowering can be explained by a reduction in

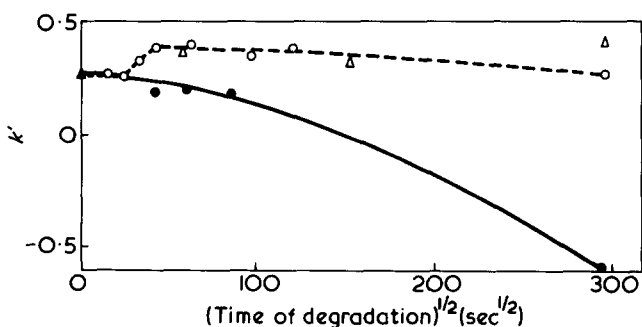


Figure 3 Variation in the Huggins constant, k' , with the square root of the time allowed for degradation for alkali concentrations of: \circ , 0.05 g/dm^3 ; Δ , 0.10 g/dm^3 ; \bullet , 0.5 g/dm^3 ; \blacktriangle , undegraded sample

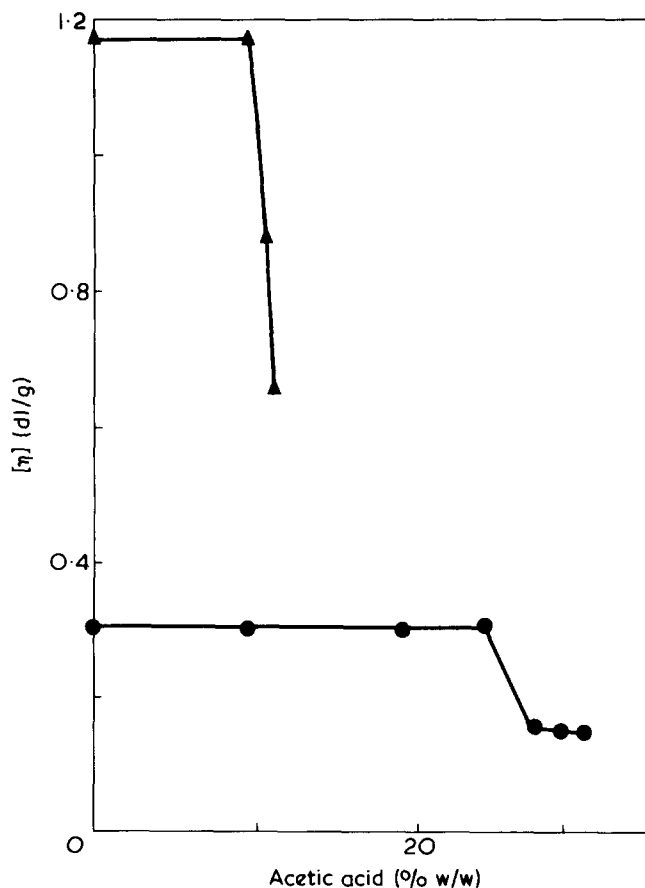
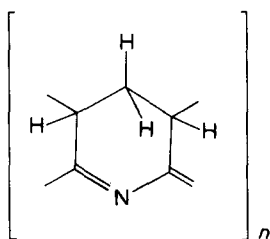


Figure 4 Variation in intrinsic viscosity of polyacrylonitrile in dimethylformamide on addition of acetic acid (glacial): \blacktriangle , undegraded sample; \bullet , sample degraded with 0.5 g KOH/dm³ of polymer solution for 1.6×10^5 sec

the polymer-solvent interaction. Studies on model compounds have shown that molecules of the type corresponding to the normally accepted structure of cyclized polyacrylonitrile are not soluble in dimethylformamide when n is 4 or more²⁷.



Hence polymer-solvent interactions would be reduced as the polyacrylonitrile underwent cyclization, the polymer chains would coil more tightly and $[\eta]$ would be lowered.

The subsequent increase in $[\eta]$ with respect to \bar{M}_n could arise from the increasing rigidity of the polymer chains as the number and length of the cyclized sequences increased. The unperturbed dimensions would be greater and $[\eta]$ would increase in spite of any further reduction of polymer-solvent interactions.

The number-average molecular weight of the polyacrylonitrile homopolymer before treatment with alkali was 8×10^4 g/mol. If alkaline treatment produces n' breaks per molecule, \bar{M}_n will fall to $8 \times 10^4/(n' + 1)$ g/mol. To a first approximation let us suppose that the treated polymer behaves as polyacrylonitrile and follows the Mark-

Houwink relation for polyacrylonitrile in dimethylformamide at the measurement temperature, $[\eta] = k\bar{M}_n^{0.75}$. As has been shown, this considerably underestimates $[\eta]$ after excessive reaction.

After a certain extent of reaction we have:

$$[\eta] = k [(\bar{M}_n)_0 / (n' + 1)]^{0.75}$$

thus

$$[\eta] = [\eta]_0 / (n' + 1)^{0.75}$$

where $[\eta]_0$ and \bar{M}_{n0} are the values of $[\eta]$ and \bar{M}_n of the untreated polymer. Thus,

$$n' = ([\eta]_0 / [\eta])^{4/3} - 1$$

Values of n' have been calculated on this basis. They are best shown as breaks per 10^4 of acrylonitrile residues, n . Figure 6 shows n plotted against the time of treatment with alkali. The initial slopes of these curves give a rough estimate of the rate of chain cleavage at the beginning of the reaction. These rates have been measured as 8.4, 0.70 and 0.14 breaks/ 10^6 acrylonitrile residues/sec for concentrations of alkali at 5×10^{-1} , 1×10^{-1} and 5×10^{-2} g KOH/dm³ of polymer solution, respectively. The rates are in the approximate ratios 1:5:60 for alkali concentrations in the ratios 1:2:10. This indicates an apparent order of reaction which is greater than unity with regard to the alkali concentration. The approximation that degraded polymer follows the Mark-Houwink relationship, established with undegraded polymer, will lead to a small over-estimation of the number of scissions at low extents of degradation.

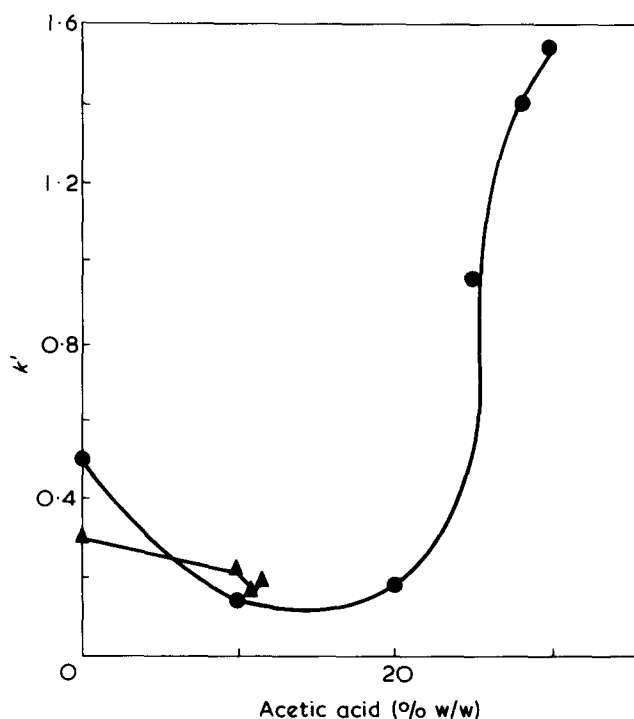


Figure 5 Change in Huggins constant k' on addition of acetic acid (glacial) to solutions of polyacrylonitrile in dimethylformamide: \blacktriangle , undegraded sample; \bullet , sample degraded with 0.5 g KOH/dm³ of polymer solution for 1.6×10^5 sec

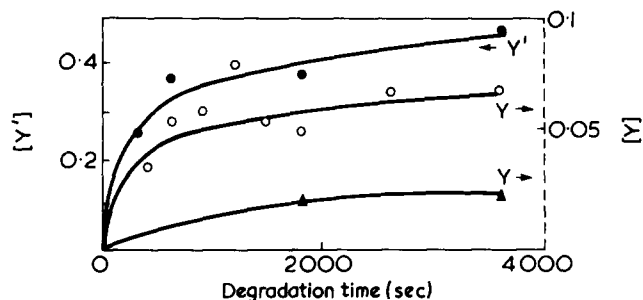


Figure 6 The variation in the number of chain breaks (per 10^4 acrylonitrile residues) with the time allowed for degradation. $[Y']$, $[Y]$ = number of breaks per 10^4 acrylonitrile residues. \blacktriangle , 0.05 g KOH/dm^3 ; \circ , 0.10 g KOH/dm^3 ; and \bullet , 0.5 g KOH/dm^3 respectively

After the initial drop in $[\eta]$, (Figure 1) there is, at lower alkali concentrations, an increase in $[\eta]$ which is followed by a further slow decrease. Some of the increase in $[\eta]$ may arise from increasing rigidity of the chains but, since \bar{M}_n increases as well, there must also be crosslinking. Extensive crosslinking is known to occur when solid polyacrylonitrile is treated thermally or treated with alkali, so it should not be thought surprising if crosslinking occurs to some extent in solution. However, the extent of crosslinking will be more limited than in the solid state because of the greater separation of the polymer molecules. The ultimate slow fall in $[\eta]$ may be the result of intramolecular crosslinking. This would give a reduced unperturbed volume for the polymer molecules. Less likely explanations include continuing chain scission or hydrolysis of the polyacrylonitrile, acrylamide or acrylic acid residues.

For a given polymer-solvent system the value of k' in the Huggins equation is constant over a wide range of molecular weights. $[\eta]$ is a measure of the hydrodynamic volume of the polymer molecules in solution. k' is an indicator of the level of interaction between the molecules in the polymer. Figure 3 shows the variation in k' with reaction time. With the highest alkali concentration (0.5 g/dm^3), k' falls steadily. However, at low alkali concentrations, the gradual fall in k' is preceded by a small rise in value. Polymer-polymer interactions become very weak. Viscometric studies on the degraded and undegraded polyacrylonitrile samples, taken in dimethylformamide/acetic acid mixtures have shown that compositions of $26.5 \pm 0.5\%$ and $11 \pm 0.5\%$ acetic acid in dimethylformamide can be considered to be theta (θ) solvents for the degraded and undegraded polymer, respectively. It is seen that acetic acid has little or no effect on the volume of the polymer molecules in the mixed solvent up to the θ point when it severely reduces the level of polymer-solvent interaction.

There is little doubt that the alkali induced modification of polyacrylonitrile in solution is a complex process involving chain scission, structure alteration and hydrolysis. Evidence for the complicated mechanistic pathways has been seen in current investigations into the changes in colour which accompany alkali induced modification and also in changes in the low temperature thermal conductivity characteristics ($0-50\text{K}$) of alkali treated samples. Details of this work will be reported in due course.

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