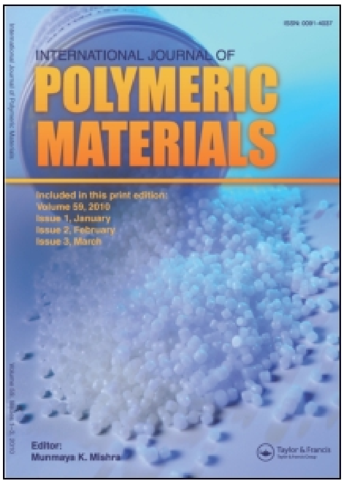

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The Nature of Color Centers in Hydrolysed Polymethacrylonitrile

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Using UV-spectroscopy, we have investigated the reactions proceeding in polymethacrylonitrile under alkali influence. It is shown that a deeply colored solution of the polymer becomes water soluble, therefore the cycles cannot be absorbing structures, as it is generally assumed. We have suggested that nitrile groups turn into carboxylates and acid groups under aqueous alkali influence. The coloration of the polymer solution is due to the formation of ionic pair multiplets. The features of their formation and destruction in various solvents are discussed.

KEY WORDS Ionic pair multiplet, color center, UV-spectroscopy, solution polymethacrylonitrile, hydrolysis

INTRODUCTION

Addition of an alkali to a polymethacrylonitrile (PMAN) solution leads to its coloration. This experimental fact was first described in References 1 and 2 over thirty years ago. It was suggested that the coloration of a PMAN solution occurred due to the nitrile group cyclization induced by the alkali. It was also noticed that the color was unstable: the solution discolored on storage for a few weeks or instantaneously after acidification.

In subsequent publications, this phenomenon was a subject of both theoretical and experimental studies. A quantum mechanical simulation of feasible absorbing structures arising in polyacrylonitrile (PAN) affected by alkali was carried out.[3] It was found that the absorption of the cyclic sequence lay in the visible region only if it contained a conjugated system ending in $N^-{:}HO{-}[C{=}N]_n{-}C{=}N^-$. A spectral study of the PMAN transformations in an alkali containing solution was made.[4] The bands in the visible region were attributed to the absorption of ionic sequences of various length. Nobody has questioned the fact that it is the cycles formation that leads to coloration of a PMAN solution.

We have obtained at least two experimental facts inexplicable in terms of nitrile group cyclization. (1) The longwave absorption ensuring coloration is obtained only if water is present in the solution. According to References 1–4, the availability of OH^- is necessary for nitrile group cyclization. It was shown in Reference 5 that

NaOH molecules dissociate in dimethylsulfoxide (DMSO), so the conditions for nitrile group cyclization are satisfied even in absence of water. Since, no coloration occurs, the absorbing structures cannot be the cycles. (2) A deeply modified polymer solution may be mixed with water: the polymer does not precipitate and the solution spectrum does not change. It is hard to imagine that the cycles should behave in such a manner.

Both facts will become clear if we assume that hydrolysis of nitrile groups occurs on addition of aqueous NaOH to a PMAN solution. It seems that coloration is impossible to explain as being due to hydrolysis, because neither carboxylates nor acid groups show absorption in the visible region. Note that a specific interaction of these groups is possible in a polymer and may result in strong bathochromic shifts of the absorption bands of cooperating groups. For example, we have found that the absorption band for nitrile groups in PAN shifts from 150 to 220 and 270 nm when their double and triple associates are formed.[6]

EXPERIMENTAL

We investigated PMAN ($\bar{M}$ = 450000) obtained by radical polymerization at room temperature. For the UV-spectroscopic study, 1% solution of PMAN in DMSO and 51% aqueous solutions of NaCNS were used. The electron spectra were recorded with a "Karl Zeis" spectrometer M-40. Aqueous NaOH (10 N) was used for PMAN hydrolysis. To study the reactions in a PMAN solution in the absence of water, dry NaOH was added to pre-dried polymer solution. Dewatering of the solution was carried out by addition of a large amount of NaCl to the reaction mixture.

RESULTS

The main features of processes occurring in a PMAN solution on alkali addition depend on the availability of water in the reaction mixture. If water is absent, there is a single band at 300 nm in the solution spectrum (Figure 1, curves 2 and 3). After water addition, bands at 350, 390 and a shoulder 410 nm appear (Figure 1, curve 4). The growth of the bands is accompanied by changes in their relative intensities. In 10 min, the 390 nm band becomes the most intense (Figure 1, curves 5–7), and this spectrum pattern is retained all the time as the bands grow.

The absorbing structures were found to be unstable in the solution. Structures with longwave absorption were destroyed more rapidly. Decrease in the band intensity at 390 nm was accompanied by an increase in the absorption near 350 and 300 nm (Figure 1, curve 8). Unfortunately, at a certain stage of the 350 nm band decrease, the soluton became opaque, and further spectral observation was impossible because of the polymer precipitation.

The total cycle of the absorbing structure formation and destruction can be observed if 51% water solution of NaCNS is used as a solvent (Figure 2). There are bands at 330, 370 and 400 nm in the PMAN spectrum in NaCNS. The substi-

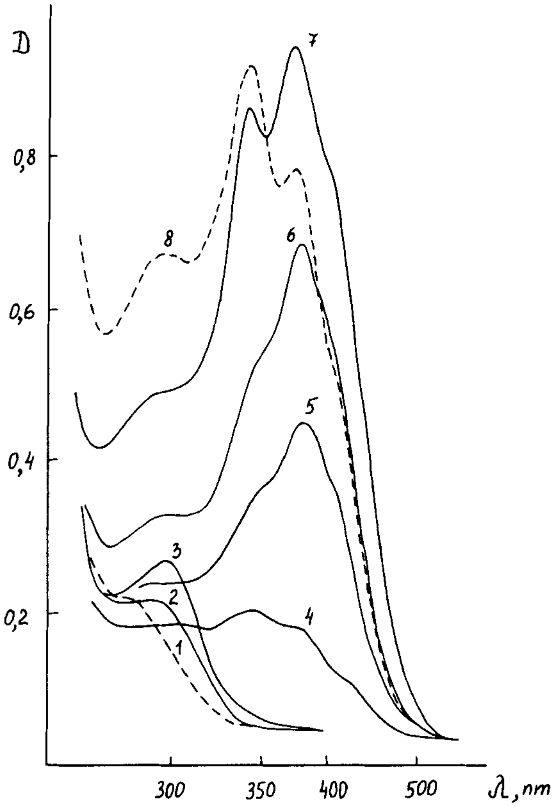

FIGURE 1 Electron spectra of 1% PMAN solution in DMSO: initial—1; after addition of dry NaOH in 5 min—2, in 3 hours—3; after addition of aqueous NaOH in 5 min—4, 10 min—5, 15 min—6, 30 min—7; after dilution with DMSO hydrolysed for a month—8.

tution of DMSO for NaCNS results in a shortwave shift of the bands: 350 → 330, 390 → 370, 410 → 400 nm. The total amount of absorbing structures formed in the PMAN solution with NaCNS is much less than in DMSO. The formation rate of absorbing structures is lower and the rate of their destruction is higher. The growth of absorption near 300 nm is terminated after the disappearance of the longwave bands. For the two months of observation, this absorption disappeared too. The spectrum became identical to the initial one.

Figures 3 and 4 show the spectra of intensely colored PMAN solutions diluted with DMSO and water. The bands at 300, 350 and 390 nm appear in the spectrum of the PMAN solution diluted with DMSO (Figure 3, curve 1). The bands at 300, 330 and the shoulder near 370 nm are observed if the solution is diluted with water (Figure 4, curve 1). Moreover, a new band at 250 nm appears which was earlier overlapped by the solvent absorption band. It is interesting to note that similar absorption near 250 nm is observed in the spectrum of the water diluted acetic acid (Figure 4, curve 2).

The dilution of the PMAN solution with water results in a rapid destruction of the absorbing structures (Figure 5). In other respects, their destruction proceeds as in DMSO. All the longwave bands decrease at first and the decrease is accom-

FIGURE 2 Electron spectra of 1% PMAN solution in NaCNS aqueous solution: initial—1, after addition of NaOH in 3 hours—2, in 1 day—3, 8 days—4, 14 days—5, 28 days—6, 60 days—7.

panied by a slight increase in the absorption near 300 nm. In addition, a considerable growth of the 250 nm band is observed. This band proves to be stable (Figure 5, curve 4).

Acidification of colored PMAN solutions in any solvents leads to their instantaneous decoloration. There is only one band near 270 nm with a shoulder near 300 nm (Figure 3, curve 2; Figure 4, curve 3).

For the verification of the reaction reversibility, we carried out a repeated alkali treatment of the solution discolored by acid. The precipitation from the solution in DMSO occurs instantaneously. The primary bands are restored in the spectrum on dilution with water (Figure 4, curve 4). A weak heating of these solutions leads to a sharp increase in the band intesity at 250 nm (Figure 6).

DISCUSSION

Hydrolysis of nitrile groups occurs in low-molecular weight nitriles in an aqueous alkali medium. The fact that this reaction occurs in nitrile polymers too would not raise any doubt if the polymer solution were not colored under alkali influence. Two-stage hydrolysis of a nitrile polymer has been suggested[7] for the explanation

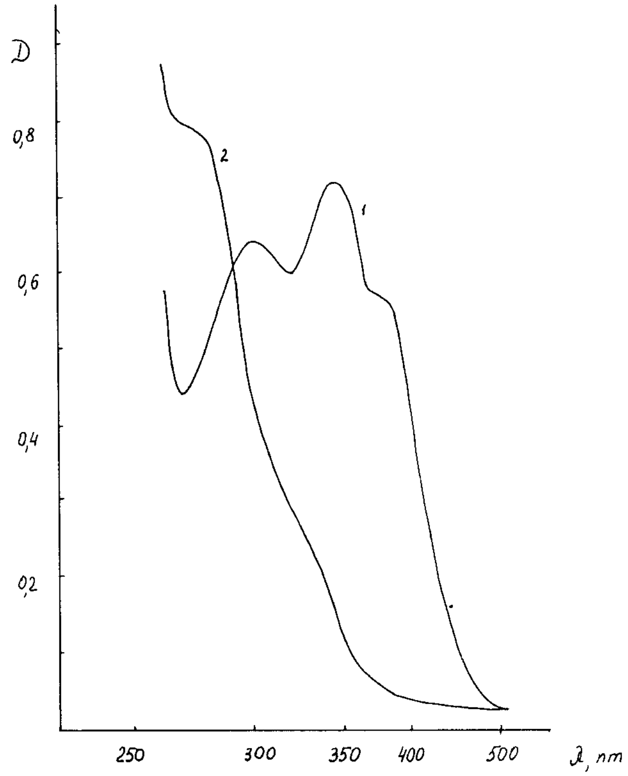

FIGURE 3 Electron spectra of colored PMAN solution in DMSO after dilution with DMSO—1, discolored by HCl—2.

of this phenomenon. The cyclization of nitrile groups is the first stage of the reactions between the polymer and the alkali (solution is colored). The hydrolysis of cyclic sequences to carboxylates is the second stage (solution becomes gradually discolored). At this stage the modified polymer becomes water soluble. Our experimental data contradict this pattern of polymer transformation because the deeply colored polymer becomes water soluble. Moreover, there are the same bands in the spectrum of diluted solution as at the initial stage of reactions (compare Figures 1 and 3). Therefore, there is no reason to suggest that the absorbing structures are altered at the profound stage of the reaction. It is the water soluble groups of the modified polymer that color the polymer solution, and this fact indicates that cycles cannot play the role of absorbing structures.

We believe that hydrolysis of nitrile groups occurs immediately on addition of aqueous alkali to the polymer solution. The 250 nm band, which appears after the dilution of the colored solution with water, should be attributed to the absorption of carboxylates. Let us remind that the weak absorption near 250 nm is found in the spectrum of acetic acid (Figure 4) and can be attributed to dissociated acid groups.

It is known[8] that hydrophilic ionic groups in polymer tend to separate from the hydrophobic polymer backbone to form ionic aggregates. We propose to assign

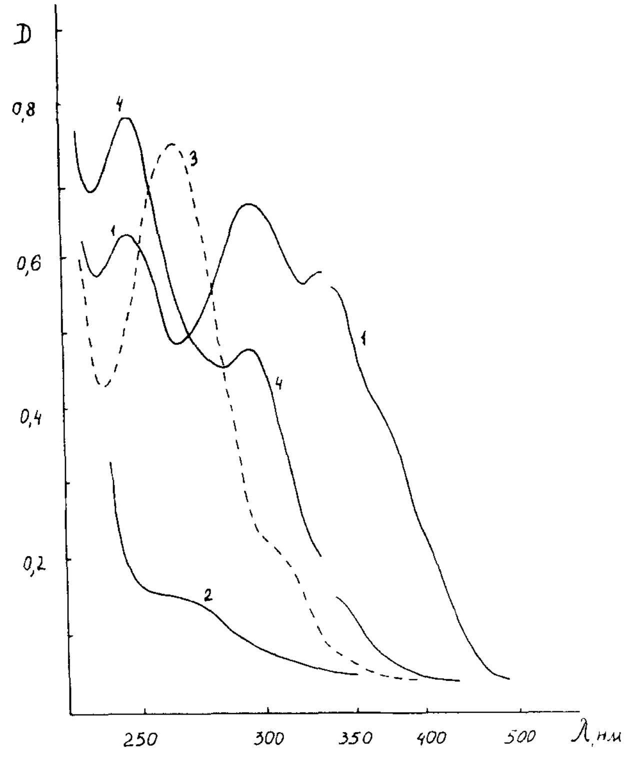

FIGURE 4 Electron spectra of colored PMAN solution in DMSO after dilution with water—1, discolored by HCl—3, after the repeated addition of NaOH—4. Electron spectrum of 10% aqueous solution of acetic acid—2.

the bands in the range 350–400 nm to the absorption of ionic clusters of different multiplicity.

Ionic clusters are a subject of an active study at present.[8,9] However, the question whether the cluster formation may be manifested in the electronic spectra has not, to our knowledge, been discussed in literature. It is obvious that a strong interaction of dipole pairs may lead to a very close contact of carboxylates, so that the overlap of their π-electron clouds becomes possible. For this reason, one may expect changes in the electronic spectrum of a hydrolysed polymer. It was shown in Reference 6 that the formation of dipole associates resulted in strong bathochromic shifts of the absorption bands. Therefore, the band shift which is observed in this case (250 → 350, 390 nm) may be due to the formation of associates with different multiplicity which hardly exceeds 4.

Discuss now the features of cluster formation when the hydrolysis of PMAN in NaCNS aqueous solution occurs. One may expect that carboxylates will dissociate in this solution and so-called polyelectrolyte effect may be observed. However, the bands of multiplets are formed with intensities less than the intensities of the corresponding bands in DMSO (Figure 2). This may be due to the drying effect of salt.[10] Actually, one can consider NaCNS as a salt added to a COONa solution

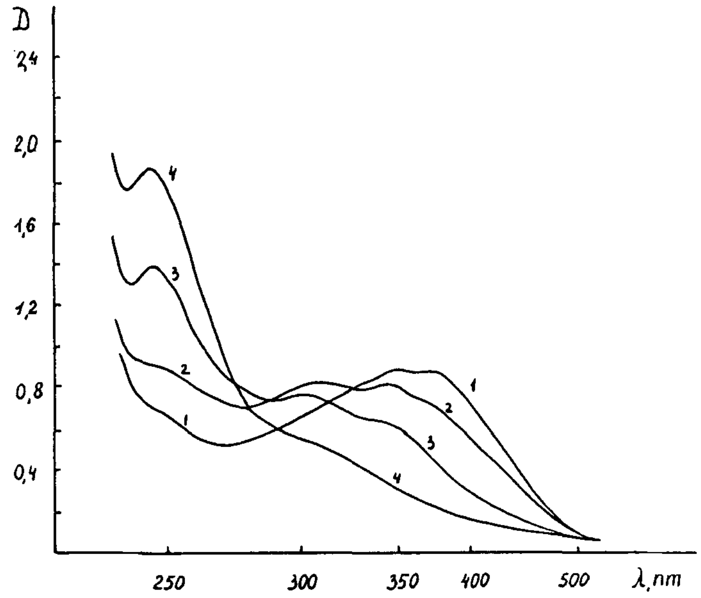

FIGURE 5 Electron spectra of colored PMAN solution in DMSO after dilution with water—1, in 4 days—2, 17 days—3, 50 days—4.

in water. It is known that if the amount of the salt added is large, COONa can exist in the solution mainly in the form of bonded ionic pairs.

Nevertheless, cluster formation in aqueous NaCNS is hindered by the solvating effect of a good solvent. The band intensities for the solution in DMSO are higher than in NaCNS. The solvation of ionic associates by water also leads to the hypsochromic shift of the absorption bands when DMSO is substituted for aqueous NaCNS, since water changes the strength of ionic crosslinks. Note that a similar shift is observed in the spectrum of the water diluted solution (Figure 4). This fact indicates that in a compound solvent, water is accumulated preferentially in the ion-rich regions.

The gradual disruption of ionic associates on prolonged storage of the solution in air can also be attributed to the solvating effect of water. The maximum rate of multiplet destruction is observed in the aqueous solution and the minimum one in DMSO (compare Figures 1 and 5). The dispersion of ionic multiplets in DMSO is promoted by water absorbed from the air, and their disruption is accompanied by a considerable increase in the absorption near 250 nm (Figure 5). This means that ionic associates in water disperse into free ionic pairs.

Acidification leads to a rapid decoloration of the solutions. A band at 270 nm appears in the spectrum (Figures 3 and 4). On repeated addition of alkali to the acid-discolored PMAN solution, the long wave absorption is restored instantaneously (Figure 4). The high rate of spectral pattern restoration evidences that the multiplets are not destroyed by the acid. The strong hypsochromic shift of the absorption bands occurs due to the substitution of a metal cation for a proton in ionic pairs. Repeated substitution of acid groups for salt groups in DMSO results in the polymer precipitation, because of a sharp increase of the salt groups insoluble

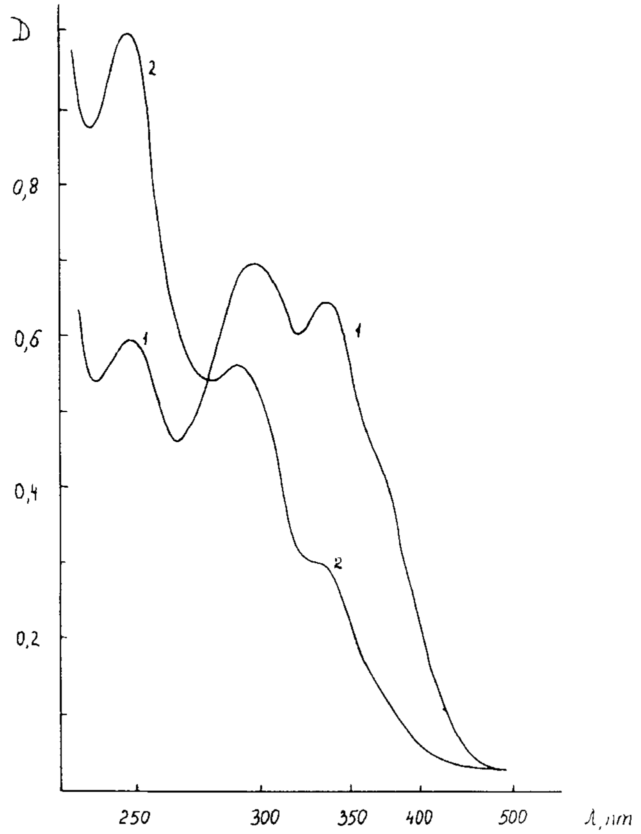

FIGURE 6 Electron spectra of colored PMAN solution in DMSO after dilution with water—1, heated at 160°C for 5 min—2.

in DMSO. In addition, decoloration is accelerated by a weak heating of the colored solutions (Figure 6). In the spectrum of the heated solution the 250 nm band is enhanced. Thus, heating leads to a breakup of ionic multiplets into free ionic pairs.

CONCLUSIONS

Analysis of available data has shown that there is no strict evidence for cycle formation in nitrile polymers treated with alkali. The authors of a recent publication[11] have come to the same conclusion. Coloration of solutions treated with alkali is the only argument in favour of nitrile group cyclization. We have found that water is necessary for the solution coloration. Besides, a deeply modified polymer becomes water soluble. We believe that hydrolysis of nitrile groups takes place in the alkali medium. The conversion of some nitrile groups to salt ones leads to a conformational rearrangement of the polymer chains. The hydrophilic salt groups tend to form ionic clusters, and this tendency is stimulated by their incompatibility with the polymer backbone and by poor solutibility in DMSO. Clustering of carboxylates leads to an overlap of their π-electron clouds, producing strong bathochromic shifts of the carboxylates bands and coloration of the PMAN solution.

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