NOTES

Dichotomies in the Viscosity Stability of Polyacrylamide Solutions. II

The viscosities of aqueous solutions of high molecular weight polyacrylamides have been observed to decrease on storage. Narkis and Rebhun[1] studied aqueous solutions of Cyanamer P-250, a high molecular weight polyacrylamide manufactured by the American Cyanamid Corp., and explained the observed viscosity decreases in terms of disentanglement of the polymer chains. Similarly, Shyluk and Stow[2] observed viscosity decreases and attributed these to a combination of disentanglement and possibly weak link scission mechanisms. Recently, we[3] have shown that these viscosity losses are the result of traces of residual persulfate polymerization initiator remaining in the polyacrylamide samples and that very high $\overline{D.P.}$ polyacrylamides can be prepared that yield perfectly viscosity-stable aqueous solutions if judicious means for polymerization initiation are employed.

When aqueous solutions of polyacrylamide are stored at room temperature, they slowly develop a haze and often a small amount of pinkish-white sediment. According to Reid,[4] if sterile water is employed for solution preparation, the pinkish sediment does not form. Also, according to Reid, microbiologic examination of this pink sediment revealed the presence of streptococci and molds. Montgomery[5] states that aqueous solutions of polyacrylamide are not subject to attack by microorganisms but will provide a substrate for the growth of mold if nutrients are present. He recommends that when solutions of polyacrylamide are stored they should contain an appropriate biocide. Aqueous solutions of polyacrylamide containing alcohol[6] or sodium nitrite,[7] present to stabilize the solutions against viscosity degradation, not only accomplish this purpose but also prevent the development of haze and sediment[3] on storage.

The production of haze and pink sediment appears to have little relationship to the viscosity degradation of aqueous polyacrylamide solutions. Solutions of high molecular weight polyacrylamides, prepared by using biacetyl and diffuse sunlight for initiation, develop haze on storage although the solution viscosity remains stable.[3] Aqueous solutions of Cyanamer P-250, however, develop haze and sediment while undergoing decreases in viscosity.

In this note we would like to report the following result. It is that the haze and/or sediment that can be centrifuged out of a stored aqueous Cyanamer P-250 solution consists in large part of poly(N-methylolacrylamide) or some very closely related material.

Two liters of a 1% aqueous solution[8] of Cyanamer P-250 was stored at room temperature for two months during which period it changed from a crystal-clear solution to a hazy solution containing a small amount of pink sediment. The solution was centrifuged, and the water-insoluble centrifugate was washed and centrifuged several times to free it from water-soluble materials. It was finally dried under less than 1 mm pressure at 45°C. The amount of isolated material represented an extremely small fraction of the original Cyanamer P-250.

Infrared spectra were taken and are presented as follows: polyacrylamide, KBr disc (Fig. 1); unknown isolated from aged Cyanamer P-250 solution, KBr disc (Fig. 2); polyacrylylglycinamide[9] containing both primary and secondary amide functions, KBr disc (Fig. 3); and poly(N-methylolacrylamide), film (Fig. 4). The latter film was prepared by adding formaldehyde (slight excess) to a dilute aqueous solution of Cyanamer P-250, adjusting the pH to 10 with aqueous sodium hydroxide, heating 1 hr at 40°C, casting, and vacuum drying at 45°C for 24 hr.

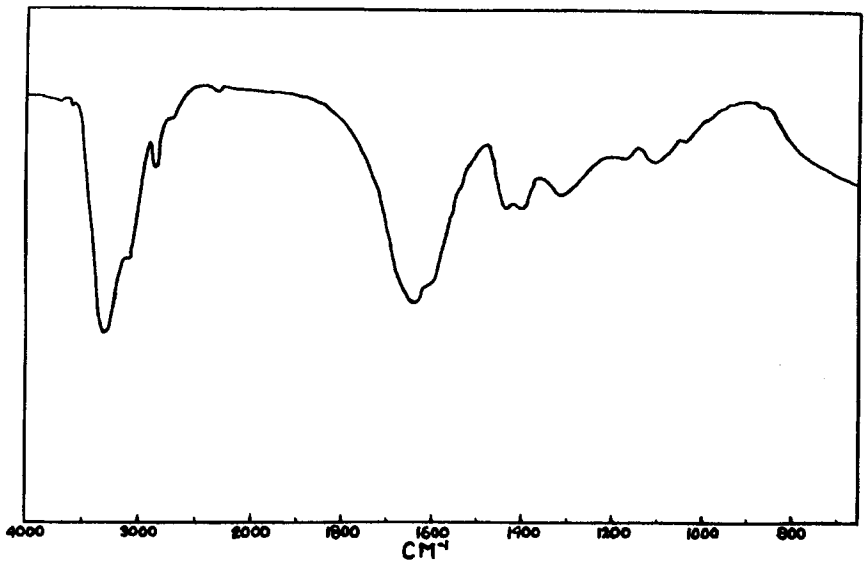


Fig. 1. Infrared spectrum of polyacrylamide, KBr disc.

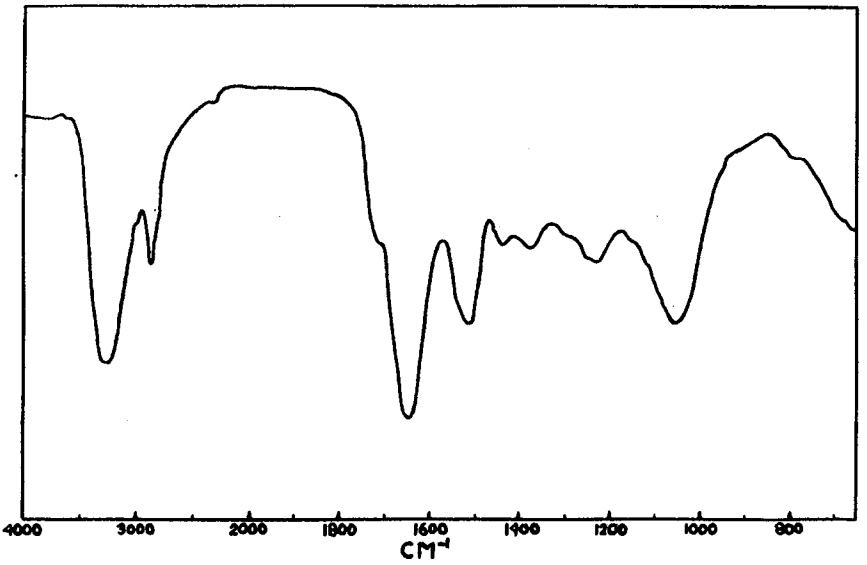


Fig. 2. Infrared spectrum of unknown isolated from aged Cyanamer P-250 solution, KBr disc.

The infrared spectrum of the unknown (Fig. 2) is vastly different from that of polyacrylamide (Fig. 1) and shows bands characteristic of polymeric secondary amides: the amide II band at 1520 cm^{-1} and the amide III band at 1240 cm^{-1}. Polyacrylylglycinamide, containing secondary amide, shows the amide II band at 1540 cm^{-1} and the amide III band at 1280 cm^{-1}. Polyacrylamide and polyacrylylglycinamide, both of which contain primary amide, show at least two —N—H stretching modes in the range

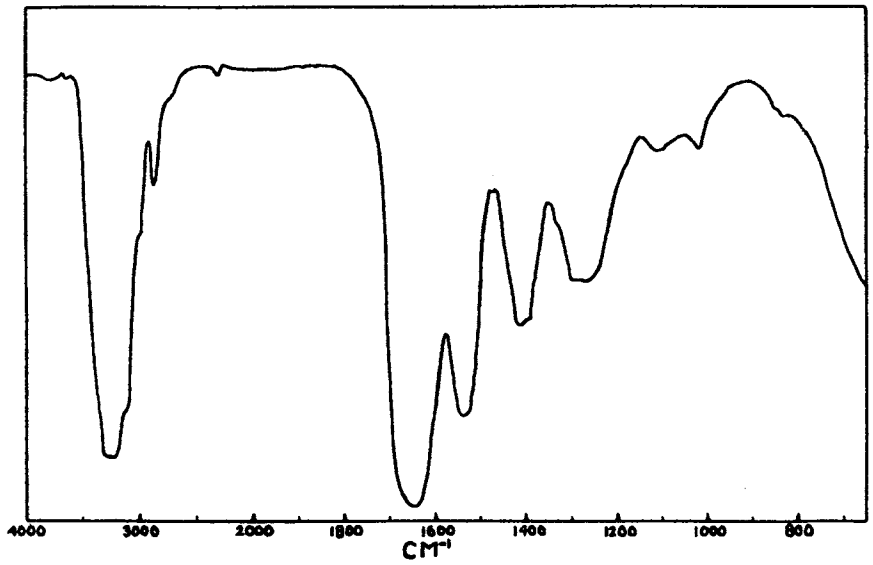


Fig. 3. Infrared spectrum of polyacrylylglycinamide, KBr disc.

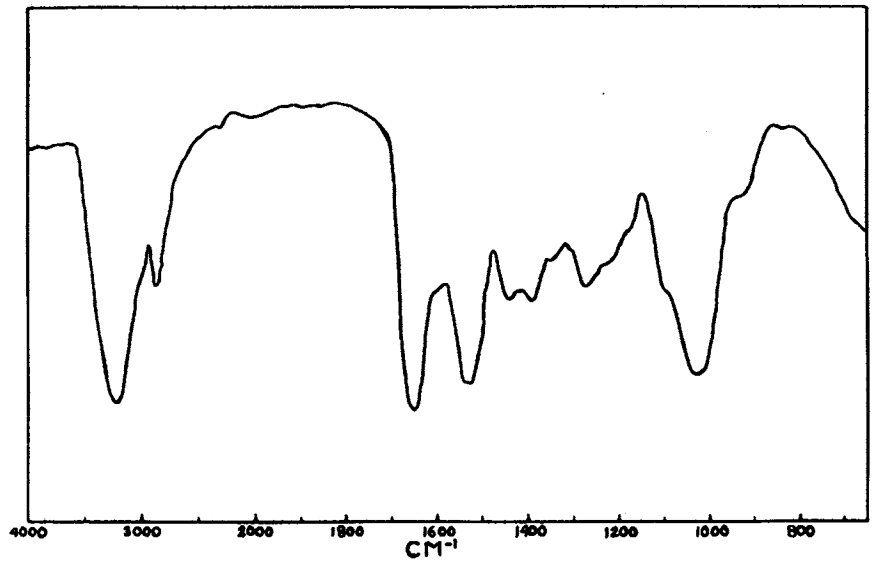
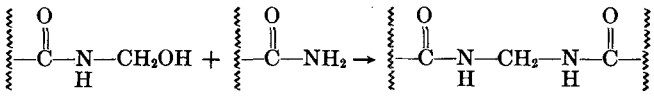


Fig. 4. Infrared spectrum of poly(N-methylolacrylamide), film.

3000–3400 cm^{-1}, whereas the unknown shows only one well-defined band at 3250 cm^{-1}. Absorption in the unknown at 1710 cm^{-1} may indicate the presence of a small amount of undissociated carboxyl groups, perhaps formed by hydrolysis during the long aqueous storage. Relatively strong absorption by the unknown at 1050 cm^{-1} is not characteristic of polyamides; and after perusal of numerous infrared spectra of related compounds such as urethanes, imides, ureas, etc., we decided that the 1050 cm^{-1} absorption must

result from the —C—O— stretching vibration of a primary alcohol. The simplest modification of polyacrylamide which could explain both secondary amide and hydroxyl functions is the conversion of polyacrylamide with formaldehyde to poly(N-methylolacrylamide). Insolubility of this product in water can be accounted for by the formation of a small amount of methylenebisamide crosslinks:



Comparison of Figure 2 with Figure 4 shows that there is a remarkable similarity between the isolated unknown and authentic poly(N-methylolacrylamide) considering that KBr disc and film spectra are being compared. Poly(N-methylolacrylamide) like the unknown shows only one well-defined —N—H stretching vibration at 3245 cm^{-1}. The amide I and amide II absorptions are essentially identical, except that amide II is not as intense in the unknown. Two absorptions near 1400 cm^{-1} are also very similar. Small differences exist in the amide III and —C—O— stretching absorptions.

To pursue the subject further, the chromotropic acid spot test[10] for formaldehyde was applied to Cyanamer P-250, authentic poly(N-methylolacrylamide), and the unknown. Cyanamer P-250 gives a complete blank whereas both the unknown and poly(N-methylolacrylamide) yield strong positive tests for formaldehyde. Since methylolation is an equilibrium reaction, water allowed to remain in contact with the two latter polymers also gives a strong positive test.

The question naturally arises as to the origin of the formaldehyde. We do not know the answer. Since the isolated unknown makes up an exceedingly small fraction of the original Cyanamer P-250, it is conceivable that there is formaldehyde present in the original Cyanamer P-250 which is beyond the limit of detection by the chromotropic acid spot test. If formaldehyde is present in the Cyanamer manufacturing process, it would have to be present originally as a highly methylolated polymer. If it were present as a trace of N-methylolacrylamide prior to acrylamide polymerization, one could expect random copolymerization and not a large degree of formolation on just a few chains. At this point it should be mentioned that after centrifugation of the unknown, the polymer remaining in solution shows the normal infrared spectrum of polyacrylamide.

The other more likely possibility is that methylolation is the result of a metabolic process of some microorganism. In spite of its reputation as a biocide, formaldehyde is quite a common metabolite or metabolic intermediate in biochemical degradation.[11–14] In our system, it would seem that a polyacrylamide molecule close to or in contact with the organism acts as an efficient scavenger of the formaldehyde as it is formed.

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