

On the Reaction between Polyacrylonitrile and Hydrazine

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Polyacrylonitrile reacts with hydrazine or hydrazine hydrate. The new polymer is insoluble in all known solvents for polyacrylonitrile even at low extents of reaction. Insolubilization is caused by intermolecular reactions. The interlinking unit is 4-*N*-amino-1,2,4-triazole.

Solutions of polyacrylonitrile in dimethylformamide slowly react with hydrazine or hydrazine hydrate at room temperature. A gel gradually separates, insoluble in all known solvents for unmodified polymer. Ammonia and dimethyl amine are simultaneously formed and easily identified in the vapor phase of a closed system. At elevated temperature — 80°C — gelation is complete within 50—65 min. The reaction seems to be specific for hydrazine in the meaning that ammonia, amines and even aliphatic diamines only cause a discoloration of polymer solutions but no observable change of solubility characteristics. What is said above refers to 2 % solutions of polyacrylonitrile (red.ox.grade, aver.-visc.mol.wt. about 8×10^4), dissolved in a mixture of three parts (by wt) of dimethylformamide and one part of hydrazine (technical grade, content of hydrazine 95—97 %). The polymer dissolves in this mixture above 40°C and is stable at room temperature for several hours until the action of hydrazine is noticeable. Even at 80°C the system remains fluid until incipient gelation takes place within the last few minutes, when the gel expands to a viscous foam. The escaping gas contains ammonia, dimethyl amine and hydrazine vapor, which are partly separable in a series of cooling traps.

Identical effects have been observed for other stoichiometric ratios between reacting species and it is well established that the gel formation is not limited to the special working conditions mentioned above. Insolubilization takes place in other solvents, such as dimethylsulfoxide. The action of hydrazine hydrate is equivalent to that of hydrazine. Even solid polymer, suspended in aqueous solutions of hydrazine, is gradually converted into a reddish-orange modification, definitely insoluble in customary solvents for linear polymer. Of course this does not mean that the *extent* of reaction is the same in all these cases, yet high enough to cause insolubility even of the primary polymer particle.

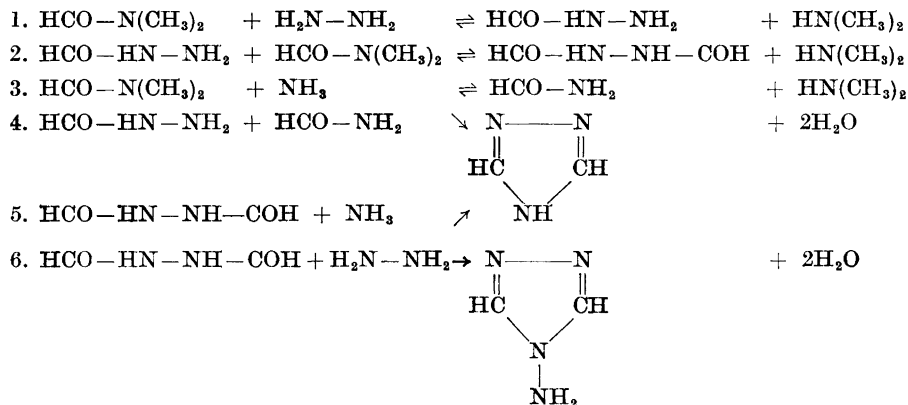
The primary gel is rubbery in character. During purification by repeated soaking in hot water and methanol (absence of air) it is gradually converted into a brittle, distinctly yellow powder. The color turns into orange on drying in air at room temperature. Contrary to standard homopolymer this final modification is resistant to alkaline hydrolysis. It evolves only a minor amount of ammonia on boiling in 10–20 % sodium hydroxide solution. The degree of swelling is low compared with the primary gel volume. Such a drastic change of physical properties might be caused by

1) a reduction of the number of solvogenic groups,

2) a decrease of the number of independent kinetic units,

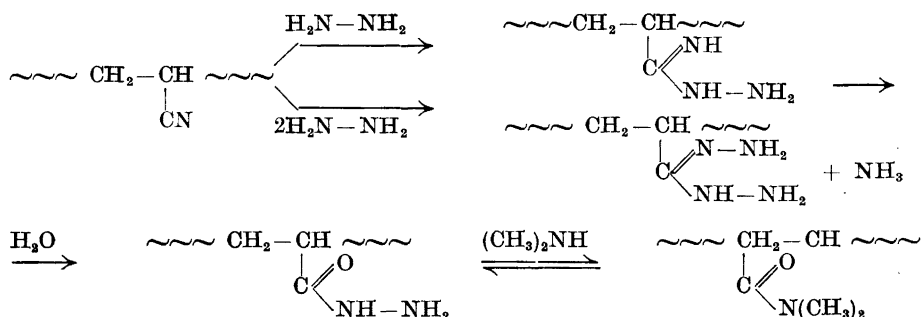
or by both cases in combination. In other words both inter- and intramolecular type reactions between polyacrylonitrile and hydrazine must be considered. However, it is equally important to pay attention to competing side reactions between solvent and hydrazine, including the contribution from water and ammonia always present in technical grades of said chemicals. The following list is given as a summary:

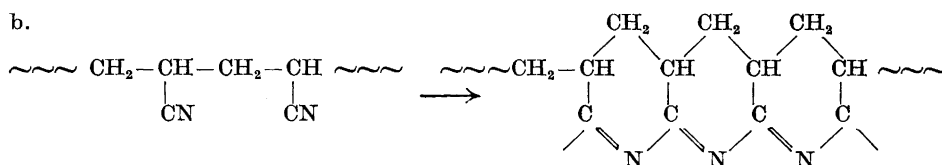
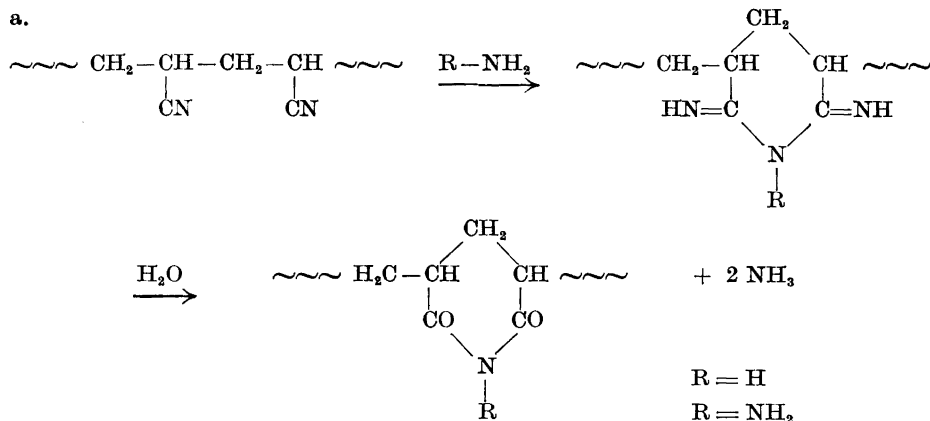
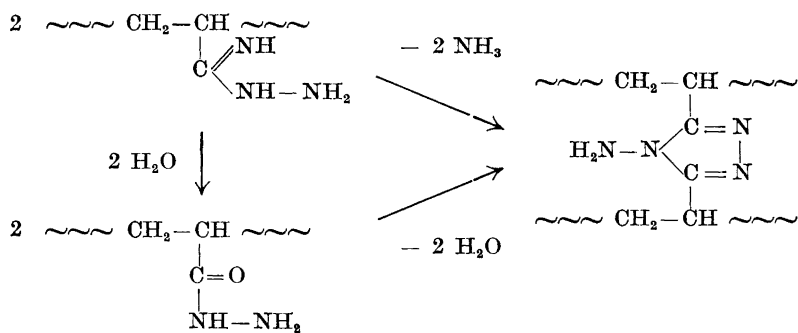
A. Interchange reactions between dimethylformamide and hydrazine:



B. Reactions between polymer, hydrazine, coreactants:

1. Hydrazidine formation, accompanied by hydrolysis and amide interchange:



2. Intramolecular cyclization at isotactic sequences ^{1,2}:3. Intermolecular reaction at random between hydrazide or hydrazidine groupings (compare case A: 4,6). The interlinking unit formed in this way is 4-*N*-amino-1,2,4-triazole:

As is seen from this survey of type reactions the formation of water is initiated by ammonia as well as of hydrazine. Water is consumed by hydrolysis of imino groups in the reacting polymer but regenerated when hydrazide groups are converted into heterocyclic units by intermolecular condensation.

The ammonia, liberated according to B:1 -3, is recycled in secondary reactions and represents a potential source of new water molecules. This explains why the rate of gelation is fairly constant even at a large change of water

content in the initial reaction mixture (*e.g.* when hydrazine hydrate is used instead of hydrazine).

The final structure of the polymer can evidently be realized in so many ways that it is hardly permitted to speak of a single, reproducible composition. This does not imply that the gelation effect is caused by all reactions between polymer and active reagents. The extent of *intramolecular* cyclization cannot be made responsible for insolubilization, as this would contradict all previous^{1,2} experience on color formation in polyacrylonitrile, caused by the action of ammonia and aliphatic amines. These chemicals do not decrease solubility of the polymer in dimethylformamide. It is much more probable that the gel effect is caused by intermolecular reactions. Insolubilization would then take place, regardless of the intramolecular balance between nitrile, hydrazidine, hydrazide and naphtyridine groupings, when the amount of interlinking units has reached, on an average, the critical value of incipient gelation. As the reaction also has been observed in the system hydrazine—solid polymer it seems permitted to anticipate its existence also in the gel phase. This only emphasizes the difficulty of obtaining a good reproducibility, as the termination of the reaction is depending on the following schedule of purification.

A crosslinked polymer, formed in this way, would act as an anion exchanger due to the presence of primary amino groups in the interlinking units. This has been confirmed by saturation with hydrochloric acid, followed by regeneration with sodium hydroxide solution and titration of liberated chloride ions. The exchange capacity amounts to 0.2—0.3 mequiv./g dry polymer in a series of six specimens. This property remains after heating the polymer at 80—100°C in strong sodium hydroxide solution. The degree of swelling increases at this saponification step, as stated above, but no dissolution of polymer has been detected.

The triazole nucleus is known to be very stable to the hydrolytic action of mineral acids. The present polymer is not dissolved by hot concentrated hydrochloric acid or by 70 % sulphuric acid. The latter is known to be a good solvent for the parent polymer. Strong nitric acid also shows good solvent properties for polyacrylonitrile and polyacrylic acid, but is incapable of dissolving the actual polymer at moderate temperatures. However, dissolution takes place rapidly in strong (60—80 %) acid at 110—115°C, apparently connected with an oxidative degradation of the sample. On dilution with water after cooling a voluminous precipitate is obtained, easily soluble in dimethylformamide. Viscosity measurements indicate a very low molecular weight. Similar effects have been obtained on samples previously reacted with nitrous acid.

Infra-red spectra of the polymers, prepared in homogeneous or heterogeneous system, show essentially the same features. Fig. 1 is a juxtaposition of relevant regions of infrared absorption for I: primary polymer, II: reacted polymer, obtained by the action of 10 % hydrazine hydrate solution in a suspension of primary polymer, III: "gel polymer", obtained from reaction in homogeneous system, followed by immediate washing and drying after insolubilization. A most striking difference is the low extent of reaction in case II and the very high one in case III, as indicated by the band at 2 260 cm^{-1} , measuring the amount of unreacted nitrile groups. The lower level,

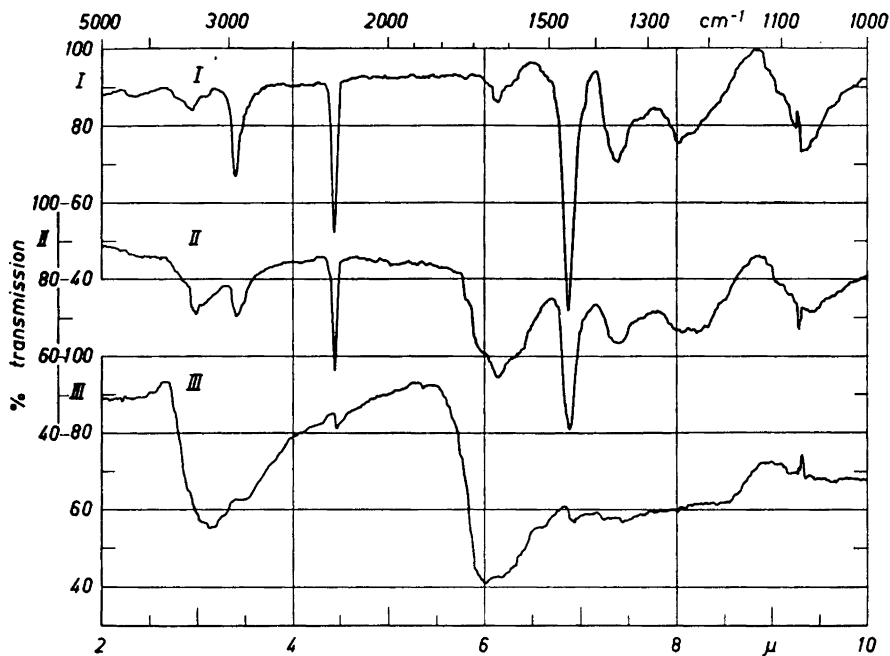


Fig. 1. Infra-red spectra of I: pure polyacrylonitrile II: polymer powder heated in 10 % hydrazine hydrate solution, III: polymer dissolved in dimethyl formamide-hydrazine, soaked after reaction in water and methanol, dried at room temperature in air.

however, is sufficient for complete insolubilization. New, broad bands arise in two regions with absorption maxima approximately at 3 and 6 μ . Their intensities are apparently related to the extent of reaction (disappearance of nitrile groups) likewise the exact location of the absorption maxima. In the case of completely reacted polymer (III) the latter band covers a variety of conceivable groupings (amides, amines, hydrazides) usually found at 1 600—1 700 cm^{-1} . The absorption maximum at 1 625 cm^{-1} is earlier¹ offered as evidence for the formation of C = N linkages in similar systems. The other (3 350 cm^{-1}) band, fairly distinct at a low extent of reaction (II), is located in the region where amino and imino groups show their stretching frequencies. The list above of type reactions would thus fit at least qualitatively into the picture obtained from the infra-red spectra. A more detailed analysis requires a variety of model substances for exact frequency determinations.

Analytical. The presence of oxygen in the final polymer (III) was confirmed by elementary analysis (Unterzaucher-Zimmermann*). The oxygen content is 13.7%. Nitrogen determination, according to Kjeldahl, was carried out on six specimens, showing a considerable scattering (12.3—13.4 %). The limiting nitrogen content after saponi-

* Carried out by Dr. A. Bernhardt, Mülheim, Ruhr.

fication at 100°C in 30 % sodium hydroxide solution is 5.1–5.5 %. Work is continued on model substances, obtained by reaction between polyacrylonitrile and hydrazine in an inert solvent (dimethylsulfoxide). This facilitates separation of the different reaction steps, ending in insolubilization, as the influence of water can be excluded. The single volatile byproduct is ammonia.

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