

Polymerization of Acrylonitrile in Suspension Systems

SVEN SÖNNERSKOG

Stockholms Superfosfat Fabriks A.B., Ljungaverk, Sweden

Present manufacturing methods for polyacrylonitrile generally involve *solution* or *quasi-emulsion* polymerisation in water due to the high solubility of acrylonitrile in the latter at elevated temperature. Continuous polymerization in solution is carried out in the presence of a water soluble catalyst and a large excess of water¹⁻⁴. Ammonium persulphate is the preferred catalyst combined with a reduction activator, such as sodium bisulphite^{1,3}. The reaction vessel should be flushed with nitrogen before the addition of freshly distilled monomer. In this way the deleterious effect of oxygen^{1,6,7} on the initiation is avoided.

Bulk polymerization is also reported in literature⁵, but at present it seems to have gained only secondary importance. As the polymer of acrylonitrile is insoluble in its monomer even at low degrees of polymerization, a stiff slurry is obtained immediately after initiation, obviously resulting in a difficult problem on heat transfer.

Suspension polymers of acrylonitrile are not earlier described, as far as known. However, polymerization of acrylonitrile in a suspension system involves no pronounced difficulties provided the following factors are considered:

1. The polymerization catalyst should be *insoluble*, in any case *inactive* in the aqueous phase, even when the water is saturated with monomer at the polymerization temperature.

2. The catalyst should be active below the boiling point of the azeotrope acrylonitrile-water (b.p. 71° C) in order to avoid working under pressure. Furthermore, increasing reaction temperature decreases the yield (conversion) of the polymer due to increasing solubility of the monomer in the aqueous phase⁸.

3. The catalyst residues remaining in the polymer particles should be volatile at the drying temperature. It is, of course, desirable that the heat stability of the polymer be affected neither by unchanged catalyst nor by compounds by side reactions in the growing polymer-monomer particle.

Most of the conditions, cited above, seem to be satisfied by the *azo* catalysts; even by the simplest one: *α,α'-azo-bis(isobutyronitrile)*. This compound may be prepared from acetone, hydrazine sulphate and sodium cyanide, as described

in the literature ^{9,10}. It is soluble and active in acrylonitrile, saturated with water, above 50° C, but inactive in water, saturated with acrylonitrile. The same applies to the analogous azo compound prepared from methyl isobutyl ketone: *α,α'*-azo-bis(*α,γ*-dimethylvaleronitrile) ¹¹⁻¹³.

In order to obtain an adjusted polymer particle size distribution during the reaction, it is necessary as usual to add a stabilizer to the aqueous phase. Almost any strongly hydrophilic polymer may be used, but three principally different cases have been observed:

1. Water soluble, non-ionic polymers, showing surface activity, for instance mixed ethers of cellulose (ethyl hydroxyethyl cellulose), act as powerful dispersing agents, resulting in small particles in the finished polymer (generally less than 0.1 mm).

2. Polyelectrolytes, such as sodium carboxymethyl cellulose and sodium polyacrylic acid, mainly function as dispersing agents only by increasing the viscosity of the water. The particle size always increases in such systems at least a tenfold compared with an analogous non-ionic, surface active system.

3. Even an *emulsifying* agent can be added to the aqueous phase, in combination with the stabilizer, to obtain a combined effect of increase in viscosity and decrease of surface tension — and still a pure *suspension* polymer is obtained. (Polymerization does not proceed in the dissolved monomer below at least 60° C.) The size of the polymer particle can in this way be regulated within wide limits.

Table 1. Polymerization of acrylonitrile with an azo activator (*α,α'*-azo-bis(*α,γ*-dimethylvaleronitrile)) in aqueous suspension in the presence of a non-ionic, surface active stabilizer (ethyl hydroxyethyl cellulose).

Apparatus: (identical for all experiments):

Three-necked flask, volume 1 000 ml, equipped with thermometer, agitator and reflux condenser. Rate of stirring 300–400 r.p.m.

Composition of reaction mixture:

Acrylonitrile	200 g
Water	600 "
Stabilizer	1.2 "
Activator	See below

Prep. No.	1	2	3	4	5	6	7	8
Activator added, g	0.5	1	2	3	0.5	1	2	3
Temp. of reaction, °C	50	50	50	50	65	65	65	65
Time of reaction, min.	240	240	210	180	180	180	180	180
Yield, g	125	145	150	142	140	155	150	140
* Average viscosity, M.W.·10 ⁻³	224	194	112	95	211	196	108	87

* K_m -value used in this table and in the following ones = $1.5 \cdot 10^{-4}$ (compare U.S.P. 2404714).

Table 2. Polymerization of acrylonitrile with an azo activator (azo-bis(dimethylvaleronitrile)) in the presence of an organic diluent.

Composition of reaction mixture:

Acrylonitrile	200 g
Water	600 "
Stabilizer: ethyl hydroxyethyl cellulose	1.2 "
Activator:	See below
Diluent:	See below

Prep. No.	1	2	3	4	5	6	7	8	9	10
Activator, g	1	2	3	3	1	1	1	1	2	3
Diluent	Kerosene	←	CCl ₄	→	←	—	Xylene	—	→	→
Amount of diluent, g	200	20	100	200	50	75	100	200	200	200
Temp. of reaction, °C	50	60	60	60	60	60	60	60	60	60
Time of reaction, min.	240	150	150	150	150	150	150	150	150	150
Yield, g	180	185	155	155	183	152	172	159	164	173
Average viscosity $M.W. \cdot 10^{-3}$	176	106	100	84	71	53	52	40	32	31

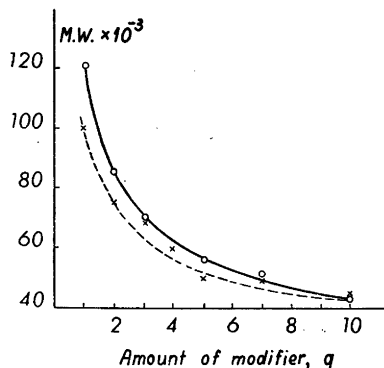
Medium polymer particle size: 0.08 mm.

The azo catalysts are soluble in acrylonitrile. The weight ratio catalyst: monomer is the main factor influencing the molecular weight, it overshadows every other variable having an effect on the scope of the reaction, even the temperature in the limited region of practical importance (Table 1). The ratio monomer: water is, of course, only of secondary importance as no reaction proceeds in the aqueous phase, but one should adjust it bearing in mind the problems connected with agitation and heat transfer during the main time of the propagation step. A ratio of 1:3 has been used during the present investigation.

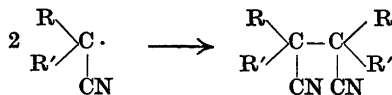
As is seen from Table 1, the average viscosimetric molecular weights are quite high even when the ratio catalyst: monomer is increased (up to 3:200). In the vinyl series considerably lower degrees of polymerization would have been expected. Addition of diluents in the monomer phase (Table 2), such as hydrocarbons or carbon tetrachloride, does not principally change this state of matters. Xylene of technical grade is an astonishing exception from this rule, however. It decreases the molecular weight of the polymer in a regular way as the concentration of the hydrocarbon in the organic phase is increased. The reason for this modifying action is not known, but it might be attributed to existing impurities in the crude isomeric mixture. The effect is not found in toluene and benzene.

Fig. 1. Relation between the average viscosity molecular weight (= M.W.) of polyacrylonitrile and the amount of modifier in the reaction mixture.

× : Ratio catalyst | monomer = 1 : 200
 ○ : Ratio catalyst | monomer = 1 : 400



The rate of this molecular dissociation is known to be essentially dependent only on the temperature so far as the energy of activation is approximately constant in a wide range of solvents¹⁵. The dissociation is not complicated by secondary or induced decomposition, but a side reaction, however, is known⁹, competing with initiation of polymerization. Part of the free radicals always coalesce forming tetrasubstituted succinonitrile:



In the ideal case when the polymer chains are initiated and terminated by identical radicals, a principal difference between suspension polymers and redox polymers should exist in the meaning that the suspension polymer, prepared by the azo catalyst, is definitely hydrophobic contrary to a redox polymer (emulsion polymer) showing strongly hydrophilic (ionic) end groups. This may be the main reason for the differences in solubility between emulsion and suspension polymers. Most solvents for polyacrylonitrile¹⁶, such as dimethyl formamide, dimethyl sulfoxide, ethylene carbonate, are hydrophilic and show negative heats of dilution in other hydrophilic low molecular weight compounds. In fact, if solvent action on the two grades of polymers is studied as recently described¹⁷, it is immediately stated that the suspension polymers are substantially *insoluble* at room temperature (solvent: dimethyl formamide) when the emulsion polymer, showing identical average viscosity molecular weight, dissolves almost *completely*, regardless of the differences in molecular weight distribution. On heating (slow heating essential, due to slow rate of dissolution) the suspension polymer dissolves completely in a narrow range of temperature situated at least ten degrees centigrade above the dissolution range of the emulsion polymer. Principally this difference exists even when the most powerful solvent, dimethyl sulfoxide, is used, but the effect cannot be observed, because every polymer investigated dissolves at 20° C — two centigrades above the melting point of the mentioned solvent!

SUMMARY

Suspension polymerization of acrylonitrile in the true sense, can be carried out, in spite of the high solubility of the monomer in water. The azo catalysts α, α' -azo-bis(isobutyronitrile) and α, α' -azo-bis(α, γ -dimethylvaleronitrile) initiate polymerization in the dispersed monomer, but not in the dissolved monomer. As dispersing agents may be used water soluble non-ionic cellulose ethers, showing surface activity, for instance ethyl hydroxyethyl cellulose. At low values of the ratio catalyst: monomer, the average viscosity molecular weights are fairly high, but they can be adjusted almost at want in a broad range by adding tertiary dodecylmercaptan to the reaction mixture. Xylene of technical grade serves the same purpose.

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