

Some Copolymers of Vinyl Alcohol-Acrylonitrile

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Copolymers of vinyl alcohol and acrylonitrile were prepared by selective hydrolysis of emulsions of the corresponding vinyl acetate-acrylonitrile compounds with ammonia at slightly elevated temperature. The presence of acrylonitrile groups in the polyvinyl alcohol chains does not lead to increased molar cohesion and a corresponding increase in filogenic properties. However, the polymers are compatible with pure polyacrylonitrile in solution (solvent: dimethyl formamide) and synthetic fibres can be prepared from such binary systems. Compared with pure polyacrylonitrile fibres the most obvious changes are the enhanced affinity for dispersed (acetate) and acid dyestuffs. The observed decrease in tenacity and increase in elongation at break is expected.

It seems hard to understand why polyvinyl acetate has never been obtained in a crystalline state when it is remembered that the polyvinyl alcohol, obtained by alkaline hydrolysis of the acetate, is often easily crystallizable. The degree of regularity in structure is almost identical in both polymers, provided that saponification is complete. The head-to-tail arrangement in the structures dominates, as is well established by degradation studies¹. One interpretation of the X-ray diffraction pattern of polyvinyl alcohol² even indicates that all of the hydroxyl groups are placed on the same side of the polymer chain. (In the light of recent investigations³ this seems far from being a general rule. The alternating distribution of the hydroxyl groups seems to be most common.) A *branching* effect is unlikely to be responsible for the poor crystallizability. It is not more probable for vinyl acetate than for other vinyl monomers — in any case it should have been indicated by a change in the physical behavior in solution. The solubility parameters E/V (cohesive energy density) and δ ($=\sqrt{E/V}$, corrected for dipole interaction related to polarizability of solvent) for polyvinyl acetate have been recently computed from molar attraction constants⁴ and found to be close to those for polystyrene or polymethyl methacrylate. This implies that special deviations from the behavior of ordinary straight polymers are not to be expected in

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solvents showing a moderate or high cohesive energy density, such as acetone (c.e.d. 4 cal.ml⁻¹ at 20° C) or dimethyl formamide (c.e.d. about 12 cal.ml⁻¹ at 20° C).

Additional studies on the crystallizability of certain types of polyvinyl alcohol copolymers⁵ are very illuminating. Generally speaking crystallization may occur, even if the second mer component is distributed at random along the head chain, provided that the side groups can be "contained" in the space unit cell of polyvinyl alcohol. This is possible with mer units such as ethylene and tetrafluorethylene, but surely not in the case of vinyl acetate.

Thus it seemed interesting to find out something about the crystallizability of the copolymers of vinyl alcohol and *acrylonitrile*. Such a copolymer is obtained by selective hydrolysis of the corresponding vinyl acetate-acrylonitrile compound. The small difference in the space occupations of hydroxyl and nitrile groups permits a cautious supposition that the conditions for crystallizability might be fulfilled in this case, at least at some proper balance between the mer units of the polymer in a highly oriented state, such as a wet spun fibre. The main point of uncertainty is whether this class of copolymers retains the fibre-forming properties found in polyvinyl alcohol and polyacrylonitrile. Several factors of steric and energetic origin influence the softening point, melting point and second order transition temperature of the finished copolymer. This needs further discussion.

As is known from earlier investigations⁶ the introduction of nitrile groups leads to increased density and a gradual increase in the intermolecular forces. This effect is, to a certain extent, counterbalanced by a melting point depression originating from the entropy changes caused by the introduction of a new structural element in the polymer chains. According to Flory^{7,8} the melting point depression $T_0 - T$ is given by the formula

$$1/T - 1/T_0 = -R/\Delta H \cdot \ln N_x$$

where R = the gas constant (in cal); ΔH = molar heat of fusion of the repeating head unit; N_x = mole fraction of the crystallizing constituent.

The formula applies to random copolymers and corresponds exactly to the classical expressions for freezing point depression and solubility-temperature gradients in dilute solutions of small molecules. For higher fractions of the new mer unit the cited formula evidently represents an oversimplification, but indicates that the melting point depression is mostly dependent upon the molar heat of fusion of the main repeating unit. It can be generalized by taking into account the interaction parameter between solvent and solute⁹. The molar heat of fusion of vinyl alcohol is not known — the simplest assumption is that it approximates the value for acrylonitrile. In the case of straight acrylonitrile polymer the large melting range (softening and decomposition)⁸ indicates a high molar heat of fusion and a low entropy of fusion — the ratio between these magnitudes represents the hypothetical melting point T_0 of the crystalline polymer. A high heat of fusion means a low melting point depression on the introduction of a second component. From thermodynamic viewpoint this only indicates limited flexibility of the molecular chains in the liquid state, possibly originating from repulsion between identical groups *along* the same chain⁸. But conditions are obviously different in a polymer where two mer

units are randomly distributed. The repulsion effect must be changed in some way, usually giving a more flexible molecule, capable of curling in the melt¹⁰. In this way the entropy change on melting is considerably increased and, for a given heat of fusion, the melting point is lowered in relation to the entropy gain. It seems probable already from these considerations that the second order transition range of the vinyl alcohol-acrylonitrile polymers is far below 100° C, because this magnitude generally follows the first order transition according to the Beamans rule¹¹, $T_{\text{melting}}/T_{\text{sec. order trans.}} = 1.5$.

EXPERIMENTAL

Preparation of the copolymers. The copolymers of acrylonitrile and vinyl acetate are easily prepared in emulsion systems. The dispersions show very good heat and frictional stability, unlike the corresponding polyacrylonitriles where stable emulsions are rare. It is apparent that the dispersed state offers the most convenient medium for the selective hydrolysis of the acetyl groups. In fact preliminary tests showed that a careful hydrolysis (pH 10, temp. 65° C, time 120 min) in the presence of (excess) ammonia did not attack the nitrile groups, as a blank of pure polyacrylonitrile immediately showed, but gave an acetyl content of the saponified copolymer usually below 0.75 %.

Table 1. Copolymerization of acrylonitrile-vinyl acetate.

Apparatus: 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: Water 1 500 g; Activator: potassium persulphate 6 g; Emulsifier: Sodium lauryl sulphate 8 g; Amount of monomers 240 g; Ratio of monomers: See below; Time of reaction 120 min; Temp. of reaction 65–70° C.

Note. The reaction mixture was flushed with nitrogen before initiation of polymerization. The monomers were mixed and dispersed in the aqueous phase at room temperature before adding activator. After reaction, excess of monomer was removed at 65° C in vacuum using a slow current of nitrogen through the emulsion.

Prep. No.	1	2	3	4
Vinyl acetate, g	40	75	120	180
Acrylonitrile, g	200	165	120	60
mole ratio				
vinyl acetate/acrylonitrile	0.12	0.29	0.62	1.85
acetyl content of saponified polymer, %	0.81	0.44	1.19	1.01
Solubility of saponified polymer in	Clearly soluble, 20 % solutions are easily prepared			
a. Dimethylformamide				
2. Acetone	Insol.	Insol.	Sol.	Sol.
Av. visc. molecular weight in dimethylformamide *	78 000	57 000	42 000	37 000

* Calculated from a speculated K_m -value of 1.5×10^{-4} , and approximating the shape exponent in $[\eta] = K \cdot M^a$ to unity.

Remarks. The polymers obtained are all somewhat sticky when heated above 50° C. It is therefore necessary to carry out the precipitation of the hydrolyzed polymer emulsion at a low temperature — preferably below room temperature. If this direction is observed the polymer is obtained as a finely divided powder — similar in appearance (and colour) to sawdust.

VISCO-ELASTIC BEHAVIOR OF THE SAPONIFIED POLYMERS

After drying at 50° C, the polymers were dissolved in dimethylformamide at room temperature. Solutions containing 10 % polymer were easily filtered through sheets of cotton linters. The de-aired dopes were spread on glass plates and the solvent removed by drying at 100° C. The films were cut into strips and oriented by stretching over a hot surface. Some observations should be mentioned here:

1. At higher acrylonitrile contents (prep. 1—2) plastic flow on stretching occurs above 50° C, the oriented films being split into fibrilla in the flow direction by a high instantaneous load. The creep recovery is low after the stretching operation. The elongation on rupture at 20° C is about 20 %. A stretch ratio of 1 : 4 is obtainable in both specimens.

2. At lower contents of acrylonitrile (prep. 3 and 4) a creep recovery on stretching was detectable. Oriented films are not split into fibrilla by a sudden heavy load, on the contrary a pronounced rubbery character is apparent. Only a low resistance to plastic flow can be noticed above 50° C, indicating a *small* increase in orientation. No critical "draw limit" can be found and the typical "necking" effect on drawing has disappeared.

These observations indicate that the introduction of acrylonitrile groups into polyvinyl alcohol do not increase the fibre-forming properties. At higher contents of acrylonitrile the characteristics of acrylic fibres make their appearance, which is trivial in our present case.

Some indirect information, however, can be obtained from another aspect. It was observed that solutions of the "hydrolysed" copolymers in dimethylformamide are miscible in all proportions with solutions of pure polyacrylonitrile in the same solvent. This is to be expected, even if mutual miscibility of polymers is by no means an ordinary phenomenon. In this way a two-component fibre can be prepared where the influence of the copolymer, acting as a diluent, can be identified by comparison with the single-component fiber, prepared under identical spinning conditions. Such a test was carried out with copolymer 4, and a pure acrylonitrile polymer, in accordance with the performance described below.

It is apparent from table 2 that the copolymer mainly acts as a "diluent" for the acrylic polymer, which is reflected in the decrease in tenacity and the increase in ultimate elongation. This might partly be due to an additive effect, derived from the fact that the copolymer units interfere with the structural elements of the polyacrylonitrile, thus both preventing and retarding orientation and final crystallization to a smaller extent. In any case both effects should co-operate in changing the structural elements in the Maxwell model of the two-component fibre which corresponds with the measurements above. From this point of view one is not allowed to negate the

Table 2. Wet spinning of a two-component fibre of polyacrylonitrile and a vinyl alcohol-acrylonitrile copolymer.

Blank (Sol. I): Solution of polyacrylonitrile (av. visc. M. W. = 70×10^5) in dimethylformamide, 15 % by weight.

(Sol. II) Spinning dope: One part by weight of copolymer 4 dissolved in dimethylformamide (15 %), mixed with three parts of Solution I.

Coagulating agent: Odourless Kerosene. Temp. of coag. agent: 135° C. Type of spinnerette: Nickel, 100 holes. Diam. of holes: 0.15 mm. Stretch ratio: 8. Rate of extrusion: 80 metres min⁻¹. Washing of the fibres: Boiling water. Drying: Room temperature.

Properties of the fibres obtained:

Type of fibre	Acrylic polymer	Acrylic polymer + copolymer
Denier	122	158
Tenacity, g. denier ⁻¹	3.4	3.0
Elongation at break, %	17.1	23.6
Dyeability with dispersed (acetate) dyestuffs at 95° C*	1	3
Dyeability with acid dyestuffs at 95° C	0	2

* Figures in a relative scale:

0 = no visible sorption.

1 = visible.

2 = moderate.

3 = good.

contribution of the copolymer to the mechanical strength. The decrease in crystallizability of the main component might alone be sufficient to account for the main part of the decrease in tenacity in the two-component fibre. The increase in elasticity is a necessary consequence from high polymer thermodynamics. The enhanced affinity of the modified fibre for dispersed dyestuffs is also in agreement with the changes mentioned above.

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Received November 16, 1954.