

means of the solubility of their barium salts (Jorpes and Gardell⁷).

The anticoagulant activity was assayed by the whole blood method of Jalling, Jorpes and Lindén⁸ and by a thrombin titration method described by Quick⁹. The radioactivity was measured in a Geiger-Müller counter. The condition of infinite thickness of the preparation is not reached for the 0.1 MeV beta-radiation of ³⁵S until it has a thickness of some 30 mg/cm². As this condition could not be fulfilled with our preparation, we decided to measure the activities of 3 mg/cm². For that reason the counts of the two preparations are not quite comparable.

The amino sugar content of the two precipitates was determined according to Gardell¹⁰. Results in Table 1.

As is evident from the table a highly active barium salt of heparin was obtained. In accordance herewith it was found that the substance contained 13.2 % of glucosamine and 0.45 % of galactosamine. The ethanol precipitate contained 3.35 % glucosamine and 2.17 % galactosamine. It is not conceivable that anything but heparin could account for the radioactivity of the barium chloride - acetic acid precipitate. Consequently this infers that sulfuric acid groups of heparin can be labelled with ³⁵S.

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Note on the Rheology of Polyacrylonitrile Solutions

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Suspension polymers of acrylonitrile, prepared by the azo activator technique¹, show apparent deviations from the ordinary behaviour of redox (emulsion or solution) polymers that calls for further attention. As earlier pointed out¹ suspension polymers do not dissolve at room temperature in dimethyl formamide even in a very broad range of molecular weight. At said temperature redox polymers may show complete solubility, and solutions containing more than 15 % by weight of polymer can ordinarily be prepared. Even if the different end groups in the two types of polymers may be one reason for this anomaly, it seems to be an undue simplification to ascribe the effect entirely to the interaction between solvent and terminating groups. The final step in the kinetic scheme of polymerization is generally shared between chain coupling and disproportionation², which would mean that other end groups than those derived from the activator would be present.

Some peculiarities, connected with suspension polymerization of acrylonitrile, should be shortly emphasized. Even at low degrees of conversion the monomer droplets are converted into a porous (spongy) particle. This polymer is insoluble in its monomer, and a two-phase system is obtained, where the reaction mainly proceeds on the large interphase. The supply of monomer at the reaction centres is secured by the action of capillary forces and by diffusion. As the particle grows acrylonitrile is consumed, why the propagation rate gradually decreases. The reaction ceases asymptotically by deficit of monomer and evidently shows a fairly long step-gradually retarded due to a decreasing supply of acrylonitrile. Just as in the case of polyvinyl chloride³ an excessive branching, chain transfer and an abnormal molecular size distribution should be expected at said reaction step. If sufficient activator is present, it is permitted to ask if even a slight crosslinking takes

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place by an initiating action on traces of bifunctional impurities (e. g. divinyl acetylene) generally present in the technical grade of acrylonitrile, prepared from acetylene.

The mentioned features of the polymerization mechanism ought to influence on the physical properties of the polymer in general, but particularly on its behaviour in solution. Even low degrees of branching and crosslinking act as steric hindrances, causing deviations from the *random flight* type of molecular configuration in dilute solutions. A look upon the general theory on the properties of macromolecular substances in solution, developed by Kirkwood ^{4,5}, Riseman ⁶, and Flory ⁷, seems to be appropriate here. The intrinsic viscosity, $[\eta]$, of a polymer is stated to be a linear function of the effective volume of the separate molecular coils in dilute solution. Thus, if \bar{r}^2 is the mean-square end-to-end distance of the coil, the following relation applies:

$$[\eta] = \Phi \cdot (\bar{r}^2)^{3/2} / M \quad (1)$$

where M is a measure of the molecular weight of the polymer, Φ a universal parameter (approximative value $2 \cdot 10^{21}$, τ being expressed in cm and $[\eta]$ in decilitres per gram), Apparently $(\bar{r}^2)^{3/2}$ indicates the effective volume of the molecular coil in solution. In the actual case it is preferably split into its component factors, referring to the unperturbed mean end-to-end distance r_0 and the coefficient of deformation a . This gives the key equations

$$[\eta] = \Phi \cdot (\bar{r}_0^2 / M)^{3/2} \cdot M^{1/2} \cdot a^3 \quad (2)$$

Table 2. Viscosity gradients of acrylic polymers, prepared in suspension systems. Solid contents of solutions: 18.0 %.

| Polymer | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|--------------------------|-----|-----|-----|-----|-----|-----|-----|
| Aver. visc. mol. weight. 10^{-3} | 51 | 54 | 55 | 59 | 70 | 75 | 44 | 45 |
| Temp., °C | ← Viscosity in seconds → | | | | | | | |
| 50 | 120 | 136 | 244 | 249 | 171 | 320 | 64 | 87 |
| 70 | 69 | 90 | 127 | 137 | 110 | 158 | 34 | 58 |
| 90 | 38 | 49 | 77 | 90 | 59 | 106 | 18 | 34 |
| 110 | 19 | 28 | 42 | 57 | 36 | 71 | 11 | 17 |
| 130 | 15 | 19 | 26 | 34 | 23 | 45 | 8 | 10 |
| Act. energy, cal. mole ⁻¹ × 10 ⁻³ | 6.8 | 7.2 | 7.3 | 6.5 | 6.5 | 6.4 | 6.8 | 7.0 |

Table 1. Viscosity gradient of a polymer of acrylonitrile, prepared in a redox system. Activator: ammonia persulphate-sodium sulphate. Average visc. mol. weight = 57 000. Solid content of solution: 18.0 %.

| Temp., °C | Viscosity, sec. (average from 4 measurements) |
|--|---|
| 50 | 94.2 |
| 70 | 55.6 |
| 90 | 34.2 |
| 110 | 21.6 |
| 130 | 14.4 |
| Activation energy of flow, cal. mole ⁻¹ | |
| 6.1 × 10 ³ | |

or

$$[\eta] = K \cdot M^{1/2} \cdot a^3 \quad (3)$$

where $K = \Phi \cdot (\bar{r}_0^2 / M)^{3/2}$. The magnitudes K and a are in general dependent of the temperature. By differentiating the logarithms of eq. (3) we obtain

$$\text{dln } [\eta] / \text{dT} = 3 \text{dln } a / \text{dT} + \text{dln } K / \text{dT} \quad (4)$$

which reveals that the intrinsic viscosity gradient is mainly determined by the change of the factor of expansion a with temperature. If steric hindrances are present, we should expect an abnormal increase in the value of a , as all effects implying hindrances to free rotation expand the chain to a larger configuration ⁸. The

corresponding influence on the magnitude $[\eta]$ was earlier implicitly formulated $[\eta] = K'M^a$, where the exponent is to regard as a comprehensive parameter, including deviations from "ideal" behaviour. Only at the Flory point⁹, Θ °K, intramolecular effects disappear and the relation (3) reduces to $[\eta]_{\Theta} = KM^{\frac{1}{2}}$, a formula showing a large similarity to the preceding expression.

What has been said about the intrinsic viscosity should also be valid in a qualitative sense for viscosity at higher concentrations as far as the dependence of the volume expansion factor is concerned. At a fixed concentration of the polymer in a good solvent, the viscosity gradient (or its computed equivalent, the activation energy of flow) is expected to show different values for various types of polymers where irregularities in structure cause deviations from the standard state (straight addition chains).

In accordance with the considerations above a series of suspension polymers was prepared and their viscosity-temperature gradients measured in the range 50–130° C. The activation energy of flow was computed from the Andrade⁸ formula

$$\eta = A_0 e^{E/RT} \quad (7)$$

giving the value of E as the slope of the straight line

$$2.3 \log \eta = \log A + E/R \cdot (1/T)$$

where the viscosity value may be expressed in arbitrary units. The explicit value of the activation energy is preferably written

$$E = 4.6 \Delta \log \eta / \Delta (1/T) \text{ cal. mole}^{-1} \quad (8)$$

Experimental. Eight polymers were prepared in accordance with the method earlier described¹, using azo-bis (isobutyronitrile) as an activator and tertiary dodecylmercaptan as a modifier*. The average viscosity molecular weight was varied in the desired range ($44 \cdot 10^3$ – $75 \cdot 10^3$) by using different amounts of the modifier. Solutions of the polymers were prepared by wetting the granules at 20° C with the required amount of dimethyl formamide for at least ten minutes. On slow agitation the slurry was gradually heated to 80° C, where dissolution is complete within 60 minutes.

* In the present investigation acrylonitrile from acetylene was used throughout all polymerizations. Average content of divinyl acetylene: 260 p. p. m.

Dilute solutions can be prepared already at 40–45° C, but practical difficulties (high viscosity, slow rate of swelling) makes dissolution at higher temperatures more attractive in the actual case. A concentration of 18.0 % was chosen. This value seems roughly to be comparable with the value 17.8 %, used in a recent investigation⁹, as the suspension polymer contains residues of activator and modifier, which are more difficult to remove by washing than water soluble catalysts. In the cited study⁹ an activation energy of flow of 5 700 cal. mole⁻¹ was found, measurements being made in the Jullander consistometer at small angles of shear. In the present case some direct reference measurements were carried out on a redox (emulsion) polymer, synthesised in the laboratory. The general features of redox polymerization are described elsewhere^{1,3}; the most important point in this connection is to observe that the reaction is terminated (interrupted) as soon as the amount of monomer present is insufficient to maintain saturation in the aqueous phase.

The viscosity gradients of the redox polymer and the suspension polymers are found in Tables 1 and 2, respectively. All measurements of viscosity were carried out in test tubes of 200 mm measuring range (diameter 20 mm, falling ball method). A lot of 15 balls (stainless steel, diameter 2.0 mm) were selected from a larger assortment and calibrated in a filtered dope of polyacrylonitrile at room temperature. Heating of the test tubes was arranged in a thin, light lubricating oil and the temperature measured at the centrum line of the tubes.

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