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Molecular weight and spinnability of polyacrylonitrile: control with water and 1,8-diazabicyclo[5.4.0]undec-7-ene during anionic polymerization in dimethyl sulfoxide

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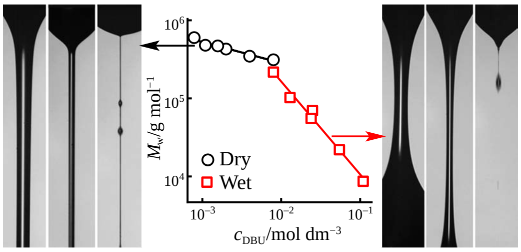
A series of linear high molecular weight acrylonitrile homopolymers have been synthesized using controlled anionic polymerization. The possibility of producing polyacrylonitrile with a wide range of molecular weights by controlling the concentrations of metal-free initiator and water has been demonstrated. The resulting homopolymers exhibit excellent spinnability.



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Polyacrylonitrile (PAN) plays a crucial role as a key industrial polymer, particularly since it is used as a precursor of carbon fibers with outstanding specific strength, stiffness and significant carbon yield during carbonization.[1,2] The characteristics of the final product are inherently shaped by the chemical structure and molecular weight of the initial polymer, which are predominantly dictated by the synthesis conditions.[3–6] Consequently, there is an urgent imperative to explore innovative approaches to manipulate polymer properties, covering aspects such as optimal polymerization conditions, solvent selection, initiators, catalysts and more.

The synthesis of PAN by anionic polymerization is characterized by high polymer yield, potential for rapid reaction rates and the ability to control molecular weight distribution.[2,7,8] The initiators of anionic polymerization of acrylonitrile are alkali metals and related compounds, such as alkoxides, amides and hydroxides.[8,9] Due to the presence of highly polar cyano groups in PAN, a homogeneous reaction occurs only in very polar solvents.[10–12] One of the urgent tasks is the search for metal-free initiators, especially for the purpose of obtaining PAN as a precursor of carbon fibers.

This work presents a methodology for the anionic polymerization of acrylonitrile[†] using an initiation system based on 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[13,14]

The results demonstrate that manipulating the initiator concentration and controlling the water content of the solvent allows one to obtain a linear homopolymer with a predetermined molecular weight.

Two series of experiments were carried out in dry and 'wet' dimethyl sulfoxide (DMSO) containing 0.0054 and 0.0654 wt% water, respectively. The DBU concentration was varied from 8×10^{-4} to 8×10^{-3} mol dm^{-3} in dry DMSO and from 8×10^{-3} to 6×10^{-2} mol dm^{-3} in 'wet' DMSO.

It was found that with increasing initiator concentration, the molecular weight of PAN proportionally decreases [Figure 1(*a*)], while the degree of branching, determined by the standard method,[15] increases [Figure 1(*b*)], but does not reach the values inherent in highly branched polymers (above 0.35). This work differs from similar ones[16] in that the influence of water and the initiator on the molecular weight characteristics of the polymer was studied. The water content in the reaction system also affects the characteristics of the polymer. Thus, a change in the concentration of the initiator in 'wet' DMSO leads to a more significant alteration in the molecular weight of PAN compared to the dry solvent, which in this case can be explained by a faster reaction of chain transfer to the polymer.

This conclusion is confirmed by comparing the nature of changes in the degree of branching of PAN under dry and wet conditions. It can be seen that the degree of branching, and therefore the rate of the chain transfer reaction to the polymer, depends on the concentration of both DBU and water in the reaction system [see Figure 1(*b*)].

Thus, by varying the concentrations of water and the initiator DBU during the anionic polymerization of acrylonitrile, it is possible to obtain a polymer with a molecular weight from tens of thousands to almost a million g mol^{-1}, having an almost linear structure.

[†] Polymerization of acrylonitrile was carried out in a two-neck round-bottom flask pre-filled with argon. A sample of DBU, dimethyl sulfoxide (50 ml) and acrylonitrile (25 ml) were sequentially added to the flask. The reaction was carried out at thermostatting (23 °C) and stirring the reagents. Upon completion of polymerization, the resulting polymer solution was poured into a large volume of distilled water acidified with hydrochloric acid. The coagulated polymer was washed on a filter with water and then dried on a rotary evaporator to constant weight.

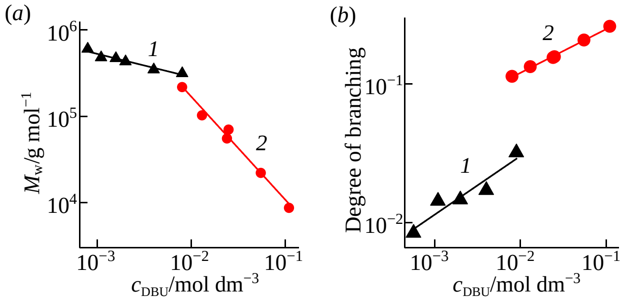

Figure 1 Effect of DBU concentration on (*a*) molecular weight and (*b*) degree of branching of PAN when the polymer was prepared (*1*) in 'dry' DMSO and (*2*) in 'wet' DMSO.

By varying the initiator concentration, a series of four acrylonitrile homopolymers with different molecular weights was synthesized. These polymers were characterized using gel permeation chromatography and capillary viscometry of dilute solutions.

Using the Huggins [equation (1)] and Kraemer [equation (2)] equations,[17] the intrinsic viscosity values for the four samples were determined [Figure 2(*a*)].

$$\eta_{sp}/c = [\eta] + K_H[\eta]^2c, \qquad (1)$$

where η_{sp} is the specific viscosity, $[\eta]$ is the intrinsic viscosity, K_H is the Huggins constant, and c is the concentration of the solution.

$$\ln(\eta_r)/c = [\eta] + K_K[\eta]^2c, \qquad (2)$$

where η_r is the reduced viscosity, and K_K is the Kraemer constant.

The values obtained by these methods are in good agreement, as evidenced by the equal values of reduced viscosity extrapolated to zero concentration. The average values are presented in Table 1.

It was observed that changes in molecular weight do not affect the K_H values, which are less than 0.5, indicating the high affinity of the homopolymers. The fact that the affinity of the polymer for the solvent remains invariant to the molecular weight of the polymer aligns well with theoretical considerations suggesting that the affinity between the polymer and the solvent is determined by the interaction of the molecular segments with the solvent, their size and chemical composition.[18]

Table 1 Characteristics of PAN samples.

Sample	c_{DBU}/ mol dm^{-3}	M_n/ kg mol^{-1}	M_w/ kg mol^{-1}	*Đ*	$[\eta]$/ dl g^{-1}	K_H	K_K	K_M
AN-1	0.003	40	87	2.2	1.6	0.47	−0.12	0.31
AN-2	0.008	82	148	1.8	2.7	0.38	−0.12	0.19
AN-3	0.004	217	469	2.2	5.1	0.40	−0.10	0.22
AN-4	0.001	344	599	1.7	6.3	0.48	−0.10	0.28

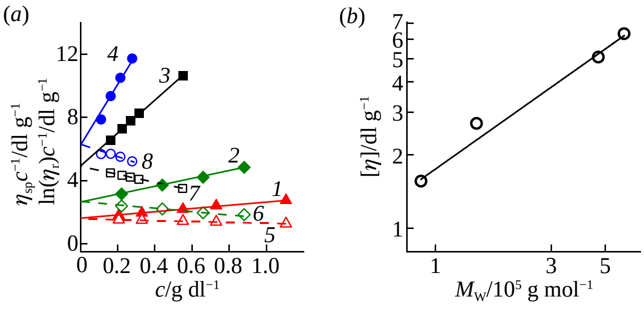

Figure 2 (*a*) Plots of (*1*)–(*4*) Huggins and (*5*)–(*8*) Kraemer equations for diluted solutions of PAN samples in DMSO: (*1*),(*5*) sample AN-1, (*2*),(*6*) sample AN-2, (*3*),(*7*) sample AN-3 and (*4*),(*8*) sample AN-4. (*b*) The relationship between intrinsic viscosity $[\eta]$ and the molecular weight of acrylonitrile homopolymers.

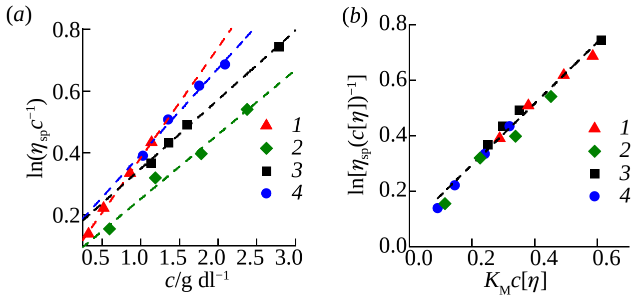

Figure 3 Determination of the Martin constant for dilute solutions of PAN samples: (*1*) sample AN-1, (*2*) sample AN-2, (*3*) sample AN-3 and (*4*) sample AN-4.

In addition to the Huggins and Kraemer equations, the Martin equation[19] [equation (3)] was used, which takes into account the volume occupied by the macromolecule in solution ($c[\eta]$).

$$\ln(\eta_{sp}/c[\eta]) = K_M[\eta]c \qquad (3)$$

The dependencies of the reduced viscosity in the coordinates of the Martin equation, which make it possible to calculate the K_M constant, are presented in Figure 3(*a*).

The use of K_M helped to level out the differences between polymers, yielding a unified relationship shown in Figure 3(*b*). This makes it possible to predict the properties of a polymer in solution until a network of entanglements is formed, based solely on its intrinsic viscosity.

The ability to stretch polymer chains when the solution jet is stretched and achieve phase separation induced predominantly by deformation is an interesting phenomenon that allows the transition from traditional wet spinning methods to non-coagulation processes with the ability to collect most of the solvent.

Until now, there have been no PAN samples with a linear structure and high molecular weight synthesized by anionic polymerization with DBU, that is, polymers with parameters responsible for good spinnability, which was tested under the condition of the onset of an entanglement network.

Using the data obtained, the concentrations corresponding to semi-dilute solutions with a developed network of entanglements were calculated as $c^{\#} = 15\ [\eta]^{-1}$ for comparison with previous studies of the spinnability of the industrial polymer.[20] This

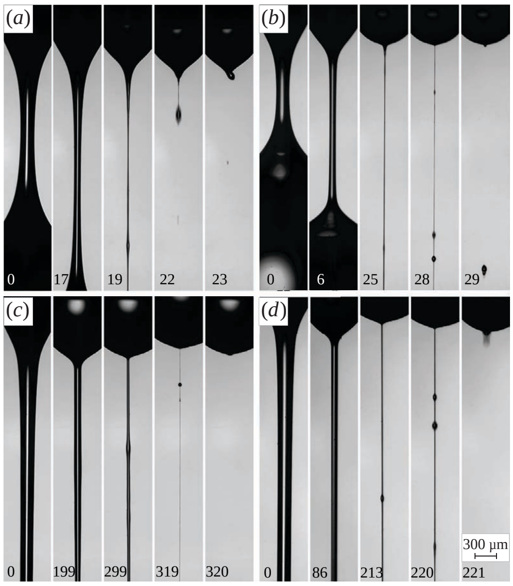

Figure 4 A series of photographs depicting the elongation of solution jets at a concentration $c[\eta] = 15$ for (*a*) sample AN-1, (*b*) sample AN-2, (*c*) sample AN-3 and (*d*) sample AN-4. The time in milliseconds is indicated at the bottom of each photograph.

Table 2 Characteristics of elongation for PAN solutions.

Sample	Concentration (wt%)	$t_{br}{}^{a}$/ms	Drops separation	Fiber
AN-c[b]	10	14	No	No
AN-1	9.6	23	No	No
AN-2	5.7	29	Yes	Yes
AN-3	3	320	Yes	Yes
AN-4	2.4	221	Yes	Yes

[a] t_{br} is the time of elongation of a solution jet with a diameter of 80 μm until the formation of a solid fiber or rupture. [b] Reference 13.

approach made it possible to investigate the fiber-forming properties of solutions under conditions of equal volume occupied by polymer coils in the solution. A series of frames reflecting the kinetics of elongational flow is presented in Figure 4.[‡]

An increase in molecular weight evidently has a positive effect on the fiber spinnability of the solutions. The solution jet of sample AN-1 with the lowest molecular weight rapidly thins due to the development of capillary instability without fiber formation in a time slightly longer than that of an industrial polymer with the same molecular weight in DMSO. Increasing molecular weight contributes to the elasticity of the polymer, leading to an increase in elongation time. For sample AN-2, the time to rupture changes insignificantly, but qualitative changes occur in the behavior of the jet, characterized by the release of solvent droplets, accompanied by the formation of a thin fiber that eventually ruptures in the region of the liquid cone at the top or bottom of the falling drop [Figure 4(*b*)]. The subsequent increase in the molecular weight of the polymer significantly increased the lifespan of the jet due to the growth of system elasticity and the slowdown in the elongation process. Despite a substantial reduction in the mass concentration of the polymer in the solution, this also led to the formation of solid fiber. The results obtained are presented in Table 2.

Thus, the possibility of synthesizing high molecular weight linear homopolymers of acrylonitrile by anionic polymerization in the presence of an initiating system based on DBU without metal-containing initiators has been demonstrated. It has been shown that an increase in the initiator concentration in the system leads to a reduction in the molecular weight of the polymer. The resulting linear acrylonitrile homopolymers with molecular weights exceeding 150 kg mol^{-1} demonstrate high potential for application in fiber spinning, as evidenced by a preliminary assessment of their spinnability.

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[‡] The elongational flow was studied in the free-fall mode of droplets (RoGER)[13] using a high-speed camera Evercam 1000-8-M (Russia) with a volumetric flow rate of 0.4 μl s^{-1} and a shooting speed of 1000 fps.