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NMR Approach to Kinetics of Polymer Ordering in Polyacrylonitrile Solutions and Acrylonitrile-Sodium Methallylsulfonate Copolymer Solutions: Solution-Concentration and Polymer-Tacticity Effects

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Abstract : Partial crystallinity of polyacrylonitrile and acrylonitrile-sodium methallylsulfonate copolymer is detected by X-ray diffraction in dimethyl formamide and glycerol-dimethyl formamide solutions in the range of polymer concentration (0.14, 0.325 mol/mol). Kinetics of isothermal ordering are followed by NMR for various temperatures, polymer concentration of the solutions and polymer tacticities. The rate of polymer ordering increases upon either a decrease of the temperature, an increase of the polymer concentration or an increase of the percentage of isotactic triads. Mandelkern's model of isothermal polymer crystallisation is applied to estimate the size of critical crystalline nuclei. Assuming that crystallites growth is negligible along polymer chain axis, one can deduce the maximal size of crystallites along this axis. The size of the crystallites perpendicularly to polymer chain axis is evaluated by X-ray diffraction. It is found to be of the order of 100 Å.

INTRODUCTION

Acrylonitrile-sodium methallylsulfonate copolymer membranes are produced for biomedical applications such as hemodialysis. The transport properties of fluids within these membranes are controlled by the internal porous morphology of the membrane. This morphology is determined by the thermodynamic transformations which lead to the formation of the porous structure from an homogeneous polymer solution. More precisely, the first step of the formation of a polymer membrane consists both in a cooling of a polymer solution and in an in-

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crease of the solution concentration by evaporation. This step may give rise to the development of a crystalline structure in the polymer solution. In this respect, the study of the ordering of polyacrylonitrile solutions (Ref. 1, 2) and acrylonitrile-sodium methallylsulfonate copolymer solutions (Ref. 3) is of crucial interest. The literature reports a specific form of crystallization for atactic polyacrylonitrile as bulk polymer or in solution (Ref. 1). Ordered domains present no chain-axis order but a lateral periodicity in the packing of rod-like chains. Bashir (Ref. 1) shows that the presence of certain solvents in an atactic-polyacrylonitrile sample can affect the crystalline structure of ordered-domains since certain solvents can co-crystallize with polyacrylonitrile. In solvent-free ordered-domains, packing is hexagonal or consists in a slight deviation from hexagonal packing. Our purpose is first to evidence the existence of ordered domains in solution, second to study the effect of temperature, solution-concentration or polymer-tacticity on the isothermal kinetics of polymer ordering in solution and third to get information about the size of ordered domains in solution.

EXPERIMENTAL

Three polymers have been used : an atactic polyacrylonitrile (PANa), an isotactic polyacrylonitrile presenting 75% of isotactic triads (PANi) and an atactic statistic-copolymer (AN-SMSa) of sodium methallylsulfonate (Na^+, $CH_2{=}C(CH_3)CH_2SO_3^-$) and acrylonitrile (CH2=CHCN) containing 3.4 mol.% of sodium methallylsulfonate. Two solvents have been used : dimethyl formamide (DMF) which is a good solvent of the considered polymers and glycerol, a bad solvent. Solutions have been sealed in glass tubes under nitrogen atmosphere. They have been homogenized by being heated and agitated at least 5 K above their melting temperature for 20 min and then cooled to room temperature. The concentration of solutions that could be prepared without polymer degradation range between 0.14 and 0.325 mole fraction. During the isothermal kinetics of crystallization samples have first been melted at 418 K for the solution of PANi (0.14 mol/mol) and at 403 K for other solutions, i.e. at least 5 K above solution melting temperature. They have then been cooled as fast as possible to the temperature of study. NMR have been performed with a Brüker CXP spectrometer working at 45 MHz. X-ray diffraction experiments have been performed on a Philips 1050/80 diffractometer.

CRYSTALLIZATION

X-ray diffraction experiments are performed for the three studied polymers (PANa, PANi, AN-SMSa) both for bulk polymers and polymers in solution. Diffraction patterns of the copolymer AN-SMSa are displayed in Figure 1. The presence of diffraction peaks in the diffraction spectra obtained for the three polymers, either in bulk or in solution, discloses the existence of crystalline domains. In all cases, the observed diffraction patterns are similar to that cited by Bashir (Ref. 1) for dry samples of atactic polyacrylonitrile. These patterns are interpreted in terms of solvent-free ordered-domains. Furthermore, it is worth noting that positions of the peaks in X-ray patterns are identical for the homopolymers and the copolymer. This result suggests that sodium methallylsulfonate monomer-units are excluded from ordered domains.

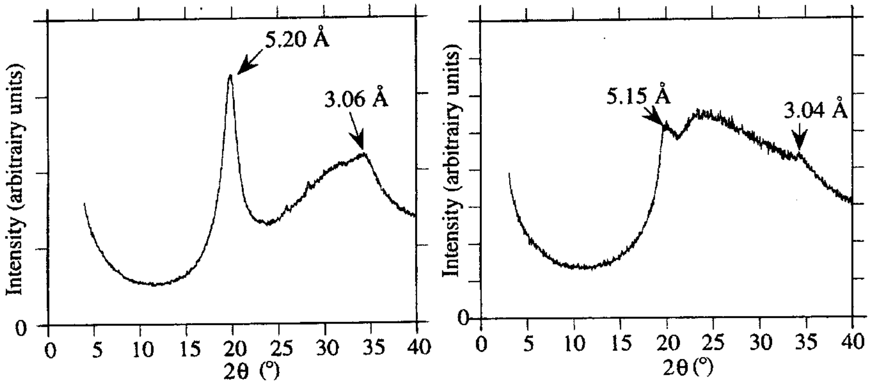

Figure 1. X-ray diffraction patterns of AN-SMSa : as bulk polymer and in solution (concentration of 0.325mol/mol, binary solvent containing 5 moles of dimethyl formamide for 1 mole of glycerol).

NMR APPROACH

The fraction of ordered polymer is determined by the measurement of the fraction of polymer in solid state which is accessible by proton NMR. The relaxation function of the protons of a polymer in solution is recorded on a sample prepared with deuterated solvent. The NMR approach is based on the differentiation of the transverse relaxation of protons located in solid-state regions (fast decay $\approx$ 50 μsec) from the relaxation of protons which belong to molecules in a viscous liquid state (long decay >> 1000 μsec). When both a solid and a liquid phase coexist in the sample, each contribution is easily quantitatively discriminated and the whole relaxation function is described as the sum :

$$Mx(t) = Xc\, Mxs(t) + (1-Xc)\, Mxl(t), \qquad (1)$$

where Xc is the fraction of protons belonging to the solid-state, Mxs(t) is the solid-state relaxation function and Mxl(t) is the liquid-state relaxation function. The whole relaxation function is conveniently fitted in order to determine the fraction Xc.

KINETICS OF ISOTHERMAL POLYMER ORDERING

The kinetics of isothermal ordering of PANa, PANi or AN-SMS in solution are observed by NMR for various temperatures, polymer concentration of the solutions and polymer tacticities. The sample is first melted and then placed in the NMR probe at the temperature of study. The transverse NMR response is recorded at regular time-intervals. For each recording, the fraction of ordered polymer (*Xc*) is deduced from fitting equation (1). Final experimental curves of the kinetics of isothermal ordering are displayed in Figure 2.

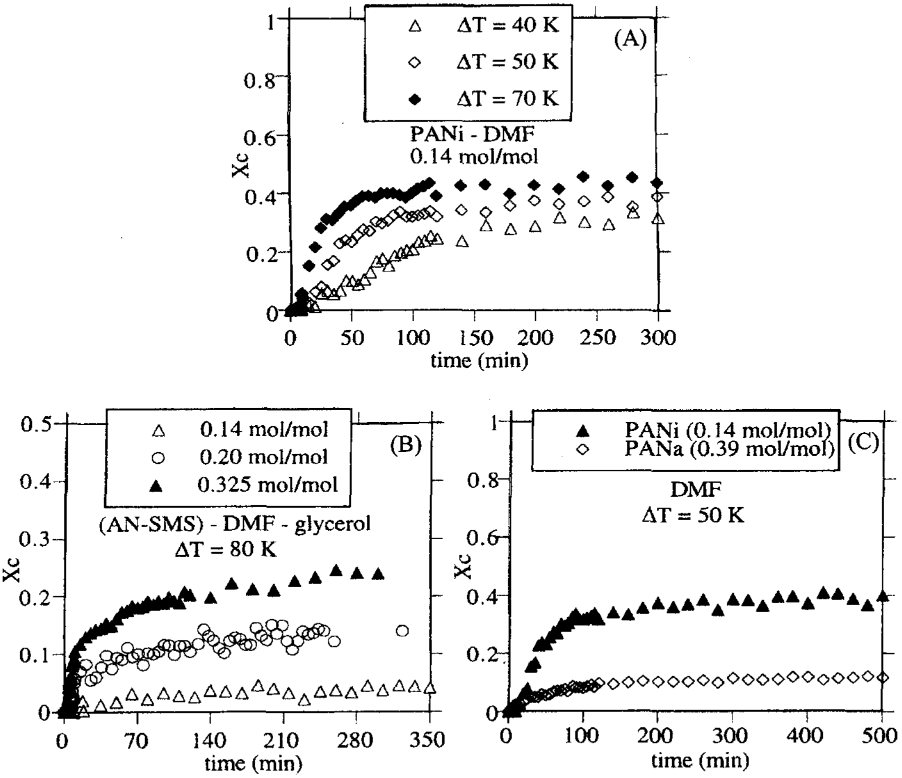

Figure 2. Kinetics of isothermal ordering of PANi, AN-SMS or PANa in solution.

The effect of the temperature on the kinetics is illustrated in Figure 2A. The parameter of surfusion (ΔT) is defined as the difference between the melting temperature and the temperature at which the ordering is studied. It is relatively low for all the experiments (smaller than 80 K). When the parameter ΔT is lower than 40 K, no crystallization can be observed even after several days. The effect of polymer concentration is illustrated in Figure 2B and the influence of the tacticity in Figure 2C. It is observed that either a lowering of the temperature or a raising of the polymer concentration in the solution or of the percentage of isotactic triads leads to accelerate the polymer ordering. This behavior is normally observed for ordinary crystallization processes in polymer systems. It is not modified by the specific crystallization of studied polymers which is limited to a lateral chain-packing. The final fraction of ordered polymer also increases with solution concentration or isotacticity.

In the light of this study, it can be concluded that the evaporation and cooling stage which initiates the process of dialysis membranes formation favors the apparition of a crystalline phase in the solution used.

SIZE OF ORDERED DOMAINS

Polyacrylonitrile ordered domains have been described as a packing of rod-like chains. It is of interest to be able to characterize the lateral dimension of the packing as well as the length of the ordered domains along the chain axis. The size of the crystallites perpendicularly to polymer-chain axis can be evaluated by X-ray diffraction with Debye Scherrer formula. It is found to be of the order of 100 Å, i.e. two orders of magnitude smaller than that reported for dilute polyacrylonitrile solutions in Ref. 4 and 5.

The kinetics of isothermal polymer ordering allow us to observe that, for each solution of study, it exists a temperature above which no polymer ordering can develop, even after several days. We propose to interpret this fact in terms of size of ordered domains. Polymer crystallization occurs in two stages : nucleation and growth. Only nuclei of a critical size (critical nuclei), or of a larger size, are thermodynamically stable. We assume that the existence of temperatures, close to the melting temperature, for which no ordering can occur is due to the fact that, at these temperatures, the size of a critical nucleus is too large compared to the size of nuclei that can actually develop. Assuming heterogeneous nucleation and a given geometry for a nucleus (a monolayer of rod-like polymer-chains), one calculates with Mandelkern's model of isothermal polymer crystallisation (Ref. 6) the size of critical nuclei for each solution and temperature studied. The size of critical nuclei perpendicularly to chain-axis is found to be very small : less than two times the diameter of a rod-like chain. It is then considered that when nuclei are smaller than the critical size, and therefore no crystallization can develop, it is because their length along chain-axis is smaller than that of a critical nucleus and not because of their lateral dimension. Furthermore, we assume that critical-nuclei growth is negligeable along polymer-chain axis because of the lack of order in this direction. The determination of the size of a critical nucleus along chain axis at the temperature above which crystallization is no longer observed therefore yields an estimate of the maximal value of the length of ordered domains along this axis for a given solution, whatever its temperature.

It is found that this length ranges in the interval [43 Å, 59 Å] for PANi, [25 Å, 33 Å] for PANa and [14 Å, 28 Å] for AN-SMSa whatever the concentration of the solution. Therefore, the maximal size of ordered domains along chain-axis increases with polyacrylonitrile isotacticity and is independent of AN-SMSa solution concentration. These results suggest that this maximal size depends only on the microstructure of the polymer.

CONCLUSION

Several conclusions can be drawn regarding hemodialysis-membrane elaboration.

First, acrylonitrile-sodium methallylsulfonate copolymer can crystallize in solution. It forms solvent-free ordered-domains.

Secondly, the process used to elaborate dialysis membranes (cooling and increase of the concentration of an AN-SMSa solution) favours polymer ordering.

Finally, solutions (and in particular AN-SMSa solutions) are found to present ordered domains of small size (of the order of 100 Å) before membrane formation. On the other hand, the final dialysis membrane is known to present polymer particles having also sizes of the order of 100 Å. This last point suggests that polymer ordering in solution influences the final polymer membrane internal morphology.

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