

Dissolution and Formation of Polyacrylonitrile in Low-Temperature Molten Salts

K. HETRICH, S. FISCHER, E. BRENDLER, W. VOIGT

TU Bergakademie Freiberg, Institut für Anorganische Chemie, Leipziger Str. 29, 09596 Freiberg, Germany

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ABSTRACT: The solubility and the polymerization of polyacrylonitrile in low-temperature molten salts was investigated. It was found, that the polymer dissolves in eutectic mixtures of molten sodium thiocyanate and potassium thiocyanate (NaSCN/KSCN) as well as in the molten hydrate lithium perchlorate ($\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$). The polymer can be regenerated by cooling the melt or diluting with water. The chemical interaction between the molten salt and the polymer was investigated by ^{13}C -NMR spectroscopy. These measurements show that the dissolution of the polymer in molten KSCN/NaSCN is accompanied by the splitting of the the hydrogen bonds. Starting from acrylonitrile, the formation of polyacrylonitrile by a radical polymerization in a molten salt becomes successful. The polymerization of acrylonitrile in an eutectic mixture of KSCN/NaSCN results in the formation of atactic polyacrylonitrile with high molecular weight. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2113–2117, 2000

Key words: polyacrylonitrile; molten salts; solvent; polymerization; ^{13}C -NMR

INTRODUCTION

Low-temperature molten salts are alternative and unconventional solvents and reaction media for polymers. Usable low-temperature molten salts can be divided into two groups, which are anhydrous molten salts and molten hydrates.

The group of the anhydrous melts is represented by eutectic mixtures of different salts with melting points below 200°C . Examples for this group are the eutectic mixtures of AlCl_3 – NaCl ($F_p = 138^\circ\text{C}$) and NaSCN – KSCN ($F_p = 127^\circ\text{C}$).^{1,2} The second group is the hydrated melts, a specific group of inorganic liquids positionable on a concentration scale of the water–salt system between concentrated salt solutions and anhydrous melts. Examples for this group are: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ($F_p = 117^\circ\text{C}$) and $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ ($F_p = 96^\circ\text{C}$).^{3,4}

The high-temperature thermoplastics polyamide 6, polyetheretherketone and polyphenylene sulfide were investigated regarding their reaction behavior with anhydrous molten salts. For these polymers, a dissolution without decomposition was found in the eutectic mixtures NaCl – AlCl_3 at 140°C and NaCl – KCl – ZnCl_2 at 220°C .⁵

For the natural polymer cellulose it could be shown that molten salt hydrates (i.e., $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$, $\text{LiI} \cdot 2\text{H}_2\text{O}$,) can be used as swelling or dissolving agents. The dissolution and regeneration of cellulose from these molten salts leads to a characteristic change of the polymer properties dependent on melt composition.^{6–8}

For the dissolution of polyacrylonitrile organic solvents (dimethylformamide, dimethyl-sulfoxide, γ -butyrolactone) or concentrated salt solutions ($\text{NaSCN}/\text{H}_2\text{O}$, $\text{ZnCl}_2/\text{H}_2\text{O}$) can be used.⁹

To improve polymer properties, the preparation of blends and graft polymers between the natural polymer cellulose, and, i.e., polyacrylonitrile is interesting. One important condition for the synthesis of blends or graft polymers is a

Correspondence to: S. Fischer.

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Table I Behavior of Polyacrylonitrile in Different Anhydrous and Hydrated Molten Salts

System	Composition (mol %)	Temperature	Behavior
NaSCN/KSCN	26.3/73.7	140°C	dissolution
LiSCN*2H ₂ O/NaSCN/KSCN	8.4/24.1/67.5	100°C	dissolution
KSCN/CH ₃ CONH ₂	26/74	30°C	partial dissolution
CH ₃ CONH ₂	—	85°C	swelling
LiClO ₄ *3H ₂ O	—	100°C	dissolution

common solvent. For the natural polymer cellulose the dissolution in the solvent system NaSCN/KSCN/LiSCN/H₂O was already discussed.⁸

For the preparation of polyacrylonitrile starting from acrylonitrile, different ways are known. The polymerization by precipitation can be carried out in substance, in salt solutions, and in organic solvents.^{10–13} Anhydrous low-temperature molten salts were never used as polymerization medium for acrylonitrile.

To find solvent systems for cellulose and polyacrylonitrile, the aim of this work was the investigation of the dissolution of polyacrylonitrile in anhydrous molten salts, especially thiocyanates and molten salt hydrates. Further, the polymerization of acrylonitrile in an anhydrous molten salt was tested, and the properties of the formed polyacrylonitrile will be discussed.

EXPERIMENTAL

For the dissolution experiments, polyacrylonitrile (Hoechst/Courtaulds) with a weight-average molecular weight of $M_w = 214,000$ was used. To test the solubility, 1% (w/w) of the polymer was given to the molten salts. By stirring the melt and polyacrylonitrile at constant temperature the behavior of the polymer was observed. After about 2 h, the molten salt was cooled down, and the salt was removed from the polymer by washing with water.

For the polymerization, 40 g of the eutectic mixture NaSCN/KSCN (26.3/73.7 mol %) was melted at 140°C. Acrylonitrile (10 g) was added to the molten salt, and the polymerization was initiated by K₂S₂O₈.

The molecular weight distribution was determined by use of gel permeation chromatography after dissolving the polyacrylonitrile in dimethylformamide.

X-ray investigations were carried out with a D5000 instrument (Siemens) with CuK_α radiation. The ¹³C-NMR spectra of the liquid samples and melts were recorded on a Bruker DPX 400 spectrometer at a resonance frequency of 100.13 MHz for ¹³C. The salt melts were sealed in a quartz tube, and DMSO-d₆ was used as external lock. The ¹³C-CP/MAS spectrum was recorded on a Bruker MSL 300 spectrometer equipped with a standard Bruker 7-mm CP/MAS probehead.

The specific surfaces of the polymers were determined with DEN-AR 1000 (Ströhlein) according to the BET method.

RESULTS

The first approach to this topic was the testing of different well-known anhydrous and hydrated melts regarding their interaction with polyacrylonitrile. The results are summarized in Table I. The dissolution of polyacrylonitrile was found in molten KSCN/NaSCN at 130°C, and in molten potassium thiocyanate/acetamide (KSCN/CH₃CONH₂) at 25°C. Molten acetamide leads to a swelling of the polymer.

Further, the hydrated molten salts LiClO₄*3H₂O and NaSCN/KSCN/LiSCN*2H₂O were tested as new solvent agents. For both hydrated melts a dissolution of the polymer can be stated. The resulting solution represents a transparent melt. The dissolution of polyacrylonitrile in these melts occurs without a decomposition of the polymer. From all discussed molten salts the dissolved polyacrylonitrile can be regenerated by cooling the melt and by diluting with water.

The structure of solid polyacrylonitrile is characterized by hydrogen bonds between the flexible α-hydrogens and the CN groups. The solvent should be able to split this hydrogen bond and to form new one.^{14–16}

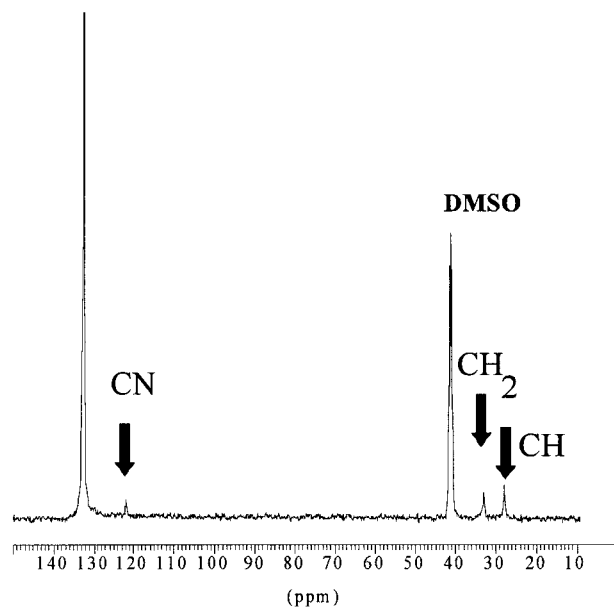


Figure 1 ^{13}C -NMR spectrum of 1%-polyacrylonitrile dissolved in molten KSCN/NaSCN at 140°C , $\text{DMSO-}d_6$ as external lock.

For further reactions of the polymer solution, the knowledge of chemical interactions between solvent and polymer is important. To describe these interaction, ^{13}C -NMR measurements of polyacrylonitrile dissolved in molten KSCN/NaSCN were carried out.

In Figure 1 the ^{13}C -NMR measurement of polyacrylonitrile in molten KSCN/NaSCN is given at 140°C . Five signals can be observed, which are at 135 ppm for the solvent anion, at 41 ppm for external standard DMSO, and for the dissolved polyacrylonitrile (121.5 ppm for CN; 27.9 ppm for CH; 34.2 ppm for CH_2). The received spectra with small signals for each of the carbon atoms of polyacrylonitrile gives evidence for the dissolution of the polymer in the molten salt.

To discuss the observed chemical shifts, ^{13}C -CP-MAS measurements on solid polyacrylonitrile and ^{13}C -NMR on polyacrylonitrile dissolved in

dimethylformamide were carried out. The resulting chemical shifts for the CH and CN groups are summarized in Table II, and compared with those of polyacrylonitrile dissolved in KSCN/NaSCN. Although it is difficult to compare the absolute values of the chemical shifts because of the differences in temperature and susceptibility, the differences between δ_{CN} and δ_{CH} of the solid polymer and of polyacrylonitrile dissolved in molten thiocyanate and dimethylformamide changed significantly.

The chemical shift for the CN group of the solid polyacrylonitrile and the product dissolved in the molten thiocyanate does not change significantly. In contrast, in a solution of polyacrylonitrile in dimethylformamide an upfield shift is observed, which is caused by a change of the coordination of the CN group in comparison to the solid. For polyacrylonitrile dissolved in the thiocyanate melt, this effect does not occur.

Because of the interaction of the SCN^- ion and dimethylformamide with the acidic hydrogen of the polyacrylonitrile, the signal for CH group is shifted upfield in both solvents in comparison to the solid.

From these data two different structures in the polymer solution can be proposed. In the case of dimethylformamide as solvent, the hydrogen coordinates to the nitrogen of the solvent.

In the thiocyanate melt, the coordination of the hydrogen by SCN^- ions must be assumed, accompanied by a coordination of the CN group by Na^+/K^+ instead of the hydrogen in the solid.

Because of the solubility of the polyacrylonitrile in the thiocyanate melt, the polymerization starting from acrylonitrile by use of a radical initiator was tested. In the following, the course of the polymerization of acrylonitrile in the NaSCN/KSCN melt will be discussed. Because of the differences of the melting temperature of KSCN/NaSCN ($F_p = 127^\circ\text{C}$) and the boiling point of acrylonitrile ($K_p = 68^\circ\text{C}$), a vaporizing of the monomer after addition to the melt was observed.

Table II Values of the ^{13}C -NMR Measurements for Polyacrylonitrile Dissolved in Molten KSCN/NaSCN, Dissolved in Dimethylformamide, and for the Solid Polymer

Measurement	Chemical Shift/ ppm —CN	Chemical Shift/ ppm —CH
^{13}C -CP-MAS-NMR: solid polyacrylonitrile	121.9	30.1
^{13}C -NMR: solution of polyacrylonitrile in molten NaSCN/KSCN, 140°C	121.8	27.9
^{13}C -NMR: solution of polyacrylonitrile in dimethylformamide, 25°C	120.4	28.5

The heat of vaporization of acrylonitrile leads to cooling and partial crystallization of the melt, whereby the degree of the crystallization depends on the addition rate of the monomer. With the addition of the initiator, the formation of the polyacrylonitrile begins at the phase boundary solid-liquid. The partial crystallization of the solvent KSCN/NaSCN is accompanied by a removing of the heat of polymerization, and can be used to control the polymerization.

The formed polyacrylonitrile dissolves immediately in the molten salt. After removing the salt from polyacrylonitrile by washing with water, the freeze-dried product was analyzed.

The X-ray powder diffraction of polyacrylonitrile prepared in the molten salt is shown in Figure 2. The polymer exhibited a diffraction peak at 16.3° , which is the typical peak for a polyacrylonitrile polymer.

For further characterization of the formed polymer, it was dissolved in dimethylformamide, and ^{13}C -NMR measurements were carried out. According to these measurements and in comparison to the literature, the polymer was found to be atactic.^{17,18}

The polymerization of acrylonitrile in molten thiocyanate results in a polymer with a high average of the molecular weight. The determined values for the weight (M_w)- and number (M_n)-average of molecular weight and the polydispersity D (M_w/M_n) are: $M_w = 1,202,000$; $M_n = 164,000$; $D = 7.3$.

The product properties were investigated using Scanning Electron Microscopy (Fig. 3) and surface determination. The morphology of the polyacrylonitrile regenerated from molten salts shows a characteristic lamellar shape. The specific surface was determined to be $31.7 \text{ m}^2/\text{g}$.

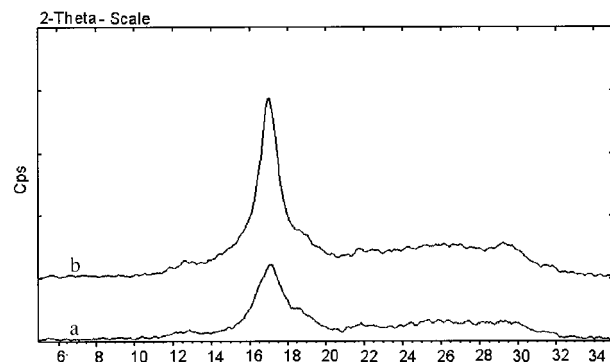


Figure 2 X-ray powder diffractions of polyacrylonitrile (a) formed in molten salt in comparison to the commercial product (b).

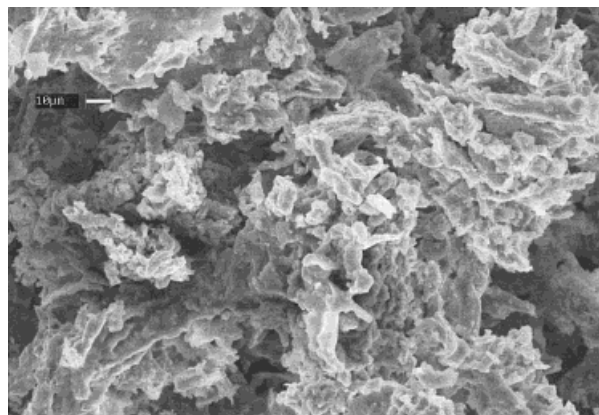


Figure 3 Scanning electron microscopy of polyacrylonitrile formed in molten KSCN/NaSCN.

The polymerization of acrylonitrile in molten acetamide/potassium thiocyanate ($\text{CH}_3\text{CONH}_2/\text{KSCN}$) at 40°C also leads to the formation of the polymer without the intermediate crystallization of the solvent. The course of the polymerization in this low-temperature molten salt is under investigation.

CONCLUSION

Polyacrylonitrile can be dissolved and regenerated in anhydrous molten salts and in hydrated melts. With the described new solvents, the number of specific polyacrylonitrile solvents is increased.

In addition, the polymer can be formed in the new solvent by radicalic polymerization of acrylonitrile in molten NaSCN/KSCN as well as in molten $\text{CH}_3\text{CONH}_2/\text{KSCN}$. The polymerization in molten NaSCN/KSCN results in polyacrylonitrile with low crystallinity and high molecular weight. An explanation for these specific product properties cannot be given yet.

In the future, the specific mechanism of the polymerization of acrylonitrile in molten salts will be investigated using molten KSCN/ CH_3CONH_2 as the solvent.

Because of the solubility in molten $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ and NaSCN/KSCN/ $\text{LiSCN} \cdot 2\text{H}_2\text{O}$, a common solvent for polyacrylonitrile and cellulose and, therefore, a possibility for the blend formation between the two polymers is given.¹⁹

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