Electrical Conductivity of Polyaniline Suspensions 2. Freezing–Melting Cycle

Jakub Wojturski,[a] *Jaroslav Stejskal,*[b] *Otakar Quadrat,*[b]
Pavel Kratochvíl,[b,*] *and Petr Sáha*[c]

[a]*Rzeszow University of Technology, 35-959 Rzeszow, Poland*

[b]*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic*

[c]*Faculty of Technology, Technical University, 762 72 Zlín, Czech Republic*

Changes in the electrical conductivity of polyaniline suspensions in 1,2,4-trichlorobenzene observed during the freezing and melting of the medium are explained by the changes in the organization of conducting particles in an electric field under a varying state of the system. The conductivity of liquid suspension is two orders of magnitude higher by comparison with the frozen one.

INTRODUCTION

Liquid systems comprising polyaniline (PANI) have been investigated mainly in connection with the processing of this electrically-conducting polymer. Solutions of PANI protonated with organic acids (*e.g.*, PANI camphorsulfonate in *m*-cresol) were used for the casting of conducting films[1,2] or for the preparation of microstructured composites with other polymers.[3,4] Preparation of dispersions composed of submicrometre PANI particles stabilized with water-soluble polymers[5–7] or inorganic colloids[8] has received considerable attention in recent years and may serve a similar purpose.[9] Surface

---

This article is dedicated to Professor Egon Matijević on the occasion of his 75th birthday.

* Author to whom correspondence should be addressed.
# For Part 1 see Ref. 19.

modification of polymer colloids[10,11] or micrometre-sized inorganic particles[12,13] with PANI has also been described. Suspensions of PANI powders in oils have been studied in relation to their electrorheological behaviour.[11,12,14–16]

In contrast to electrical properties of solid PANI, which were reported in the literature in great detail,[17] the electrical conductivity of liquid systems has been little investigated. Measurements of electrical conductivity of PANI suspensions in 1,2,4-trichlorobenzene[18,19] may serve as an example. In this follow-up study, we concentrate on the effect of the solid-to-liquid state transition on the electrical conductivity during the freezing and melting of PANI suspensions.

EXPERIMENTAL

Polyaniline

Aniline hydrochloride was dissolved in diluted hydrochloric acid, the solution was cooled to 0–2 °C, and an aqueous solution of ammonium peroxodisulfate was added. Equal concentrations of aniline salt and the oxidant (0.2 M) in the reaction medium (1 M HCl) were used. Next day the precipitate was separated, washed with dilute hydrochloric acid, followed by acetone, and dried. Polyaniline hydrochloride was ground in an agate mortar and sieved. Particles observed in the microscope have a 1–10 μm size.

Suspension

1,2,4-Trichlorobenzene (TCB; purum; Fluka, Switzerland) was selected as suspension medium, because of its close density (1.455 g cm^{-3} at 20 °C) to that of PANI hydrochloride (1.43 g cm^{-3} at 20 °C, determined from the geometry and mass of a compressed tablet). Flotation of PANI particles was thus slowed down. A freshly prepared suspension (volume fraction, φ(PANI) = 1%) was sonicated for 15 min in an ultrasonic bath (Jencons Scientific, UK) to reduce aggregation of particles.

Electrical Conductivity

A PANI suspension was placed between two aluminum blocks separated by a d = 3 mm silicon-rubber spacer (Figure 1). The electrode surface area in contact with the suspension was S = 28 cm^2. A voltage U was applied to the electrodes and the direct current I passing through the suspension was recorded with a milivoltmeter line recorder (TZ 5000, Laboratory Instruments, Czech Republic). The electrical conductivity was calculated as $\sigma = Id/US$. The conductivity of TCB at 20 °C was 20 nS cm^{-1}, and that of PANI hydrochloride 0.6–2.5 S cm^{-1} (for various batches of PANI, measured in a compressed tablet).
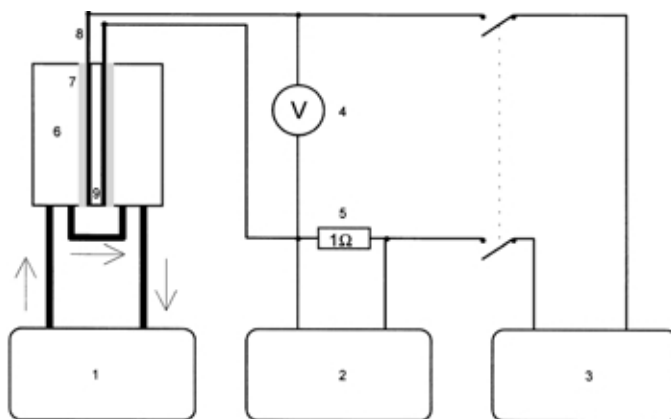
Figure 1. Set-up for the electrical conductivity measurement: 1 – thermostat, 2 – chart recorder, 3 – power supply, 4 – voltmeter, 5 – resistor, 6 – aluminium blocks, 7 – silicon rubber insulation, 8 – chromium-nickel electrode, 9 – silicon rubber spacer containing PANI suspension.

RESULTS AND DISCUSSION

Organization of PANI Particles in Electric Field

Polyaniline particles suspended in liquid TCB are partly aggregated into a loose network-like structure because hydrophilic PANI particles tend to form clusters in hydrophobic TCB (Figure 2a). When a PANI suspension is placed into an electric field, PANI particles become polarized. Interaction of induced dipoles leads to the formation of particle chains and strands of chains,[18–20] which are oriented preferentially parallel to the electric field (Figures 2b, c). The orientation improves as the electric field strength increases. Particles remain aligned, even after the voltage has been switched off, and the structure gets slowly disordered by the diffusion-controlled processes.

Electrical Conductivity of the Frozen/Melted PANI Suspension

In a typical experiment, the as-prepared suspension was frozen at 0–2 °C. Voltage was applied to the electrodes, the temperature was increased (2 °C min^{-1}) up to 45 °C. Time dependences of the conductivity (Figure 3), rather than dependences on temperature, have been recorded.

The electrical conductivity of the frozen PANI–TCB suspension is low (< 10 nS cm^{-1}) because the volume fraction, $\varphi = 1\%$, of immobilized PANI
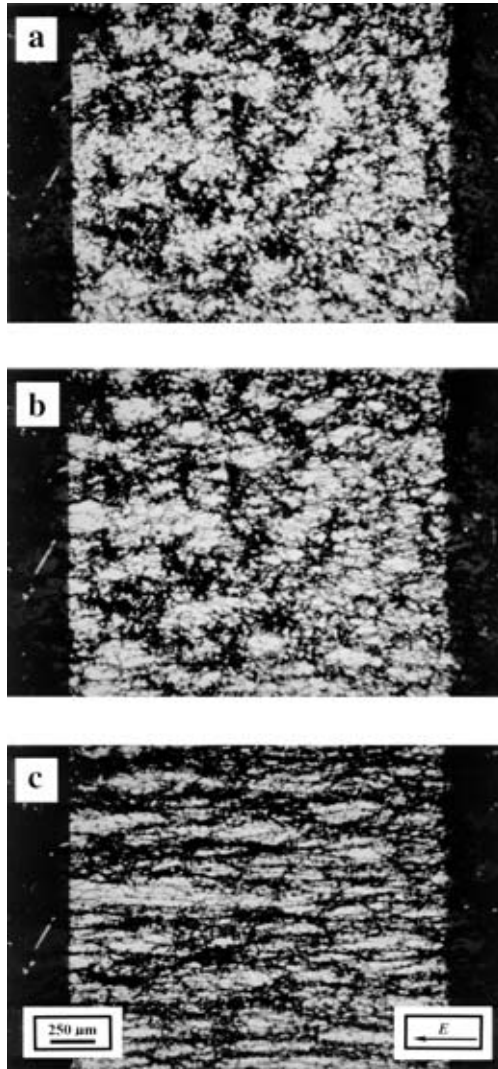
Figure 2. Organization of PANI particles ($\varphi = 1\%$) in TCB suspension placed between gold electrodes at electric field strengths of (a) 0 V mm^{-1}, (b) 25 V mm^{-1}, and (c) 90 V mm^{-1}.

particles (Figure 4a) is a much lower fraction than the percolation threshold. The percolation theory predicts, for a hypothetical system composed of randomly distributed conducting and insulating spherical particles, a 16–17% limit of conducting objects[21–23] (Scher-Zallen criterion[21]). Above this

percolation threshold, there are paths formed by conducting particles and the system conducts electric current; below this limit, the fraction of particles is not sufficient for the production of connective structure of conducting chains and the electrical conductivity is reduced by many orders of magnitude. For example, when spherical PANI particles covered by poly(vinyl alcohol) (PVAL) are similarly immobilized in a continuous insulating PVAL matrix, a percolation threshold at φ(PANI) = 8–10% has been reported.[24,25]
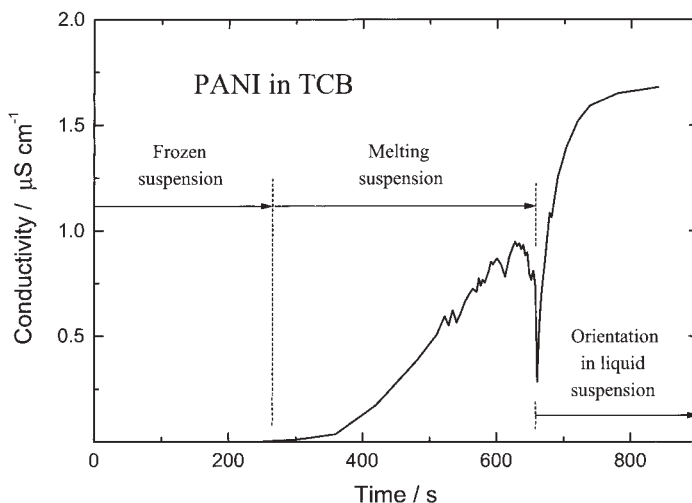

Figure 3. Electrical conductivity of PANI suspension (φ = 1%) in TCB during melting of the frozen suspension. Electric field strength, E = 13 V mm^{-1}.

As the PANI suspension in TCB gradually melts (m.p. 15–18 °C), the liquid phase fraction slowly increases. We assume that the heat evolution caused by the passing current will be centred on PANI particles and thus the TCB will preferentially melt in their vicinity. Free PANI particles in the liquid phase become partly oriented in the direction of the electric field and form conducting pathways between the melting crystals of the suspension medium (Figure 4b). Consequently, the electrical conductivity slowly increases (Figure 3). It should be noted that the electrical conductivity of PANI composites alone increases with increasing temperature[25,26] but not to such an extent to explain the conductivity changes observed here. At this stage, the output signal fluctuates (Figure 3): melting crystals of TCB are moving due to the diffusion caused by temperature gradients, and the conducting paths of PANI particles are then disturbed and recovered again by the action of the electric field.
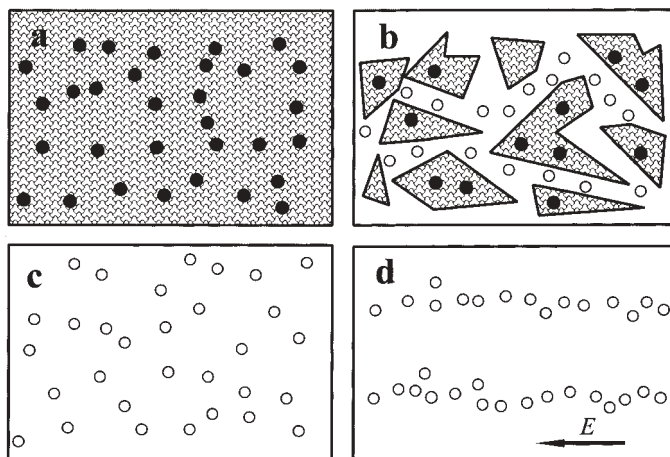
Figure 4. Schematic presentation of conducting particles in frozen suspension (a), during its melting (b), after melting in liquid state (c) and the subsequent organization of PANI particles in the direction parellel to the electric field (d). Conducting particles are either immobilized in the frozen medium (●) or free in liquid phase (○).

In the investigation of solid composites composed of PANI and an inorganic salt (ammonium sulfate), a low percolation threshold at φ(PANI) = 2.5%, *i.e.* much lower than the Scher-Zallen limit[21] for the systems of spherical particles of the same size, has been observed.[24] During the mixing of PANI powder with the salt crystals, conducting particles are not uniformly distributed, but they are forced to penetrate the space between the crystals. Consequently, they form a conducting network (visible under the microscope) at a much lower concentration as compared with the randomly distributed systems. We believe that analogous behaviour may be anticipated in the present case, when PANI particles in the liquid phase are located between the fragments of the frozen suspension. Unlike in the classical Scher-Zallen case, for small conducting particles filling nonspherical voids between large insulating objects, the percolation limit can approach zero.[23] The PANI suspension may thus, even at a volume fraction of 1%, reach and exceed still lower percolation thresholds and its electric conductivity increases.

A certain logical relation seems to exist between the present system and the behaviour of PANI networks formed in blends of PANI[3,4] or PANI dispersion particles[27,28] with various polymers due to incompatibility of polymer components. Such systems have extremely low percolation thresholds (well below φ(PANI) = 1%). Although the nature of the separation of conduct-

ing and insulating components in these two systems is different, the resulting connective conducting structure may have similar electrical properties, reflecting an extremely low percolation threshold.

After the system has completely melted (Figure 4c), the Scher-Zallen percolation limit at $\varphi = 16-17\%$ can again be anticipated[21–23] because of the nearly random distribution of conducting particles in continuous phase. That is, like in the frozen state, the system is again found to be far below such a percolation limit. Consequently, the electrical conductivity drops sharply. A distinct minimum on the conductivity–time curves (Figure 3, and also later in Figure 5) has always been observed after the suspension has melted.

In liquid TCB, PANI particles get organized in the electric field (Figure 2), and the electrical conductivity slowly increases again (Figure 3) up to a limit value (dependent on the volume fraction of PANI and applied electric field strength).[19] This increase is time-controlled, and an additional increase in temperature has only a marginal effect on the conductivity.

Freezing–Melting Cycles

In the repeated freezing–melting cycles, two cases were investigated: the first freezing of the suspension was made either in the absence of electric field (Figure 5a) or in the oriented state in an electric field.

When PANI particles are not organized prior to the solidification of suspensions, the melting behaviour of such a suspension (Figure 5a) is the same as outlined in Figure 3. After the suspension has melted, its conductivity increases as the orientation of PANI particles parallel to the electrical field proceeds. The limiting conductivity is higher than in Figure 3 because another PANI sample was used in this experiment. The decrease in temperature from 20 °C below the melting point of TCB to 8 °C is accompanied by freezing of the medium and by a decrease in the conductivity from 3 μS cm^{-1} to < 10 nS cm^{-1}, *i.e.* more than 300 times. This can partly be explained by the displacement of particles in conducting chains by the solid phase formation. The freedom of particle movement seems to be essential for the conductivity of PANI suspended in a liquid medium. In liquids, the induced dipoles organize particles into chains. Any perturbation of the connectivity of the structure is repaired by the rearrangement of particles and recovery of the network-like structure. The immobilization of particles and their inability to repair broken contacts thus seems to be the main reason for the low conductivity in the solid state. A similar decrease in conductivity has also been observed when oriented PANI particles were petrified in the forming poly-
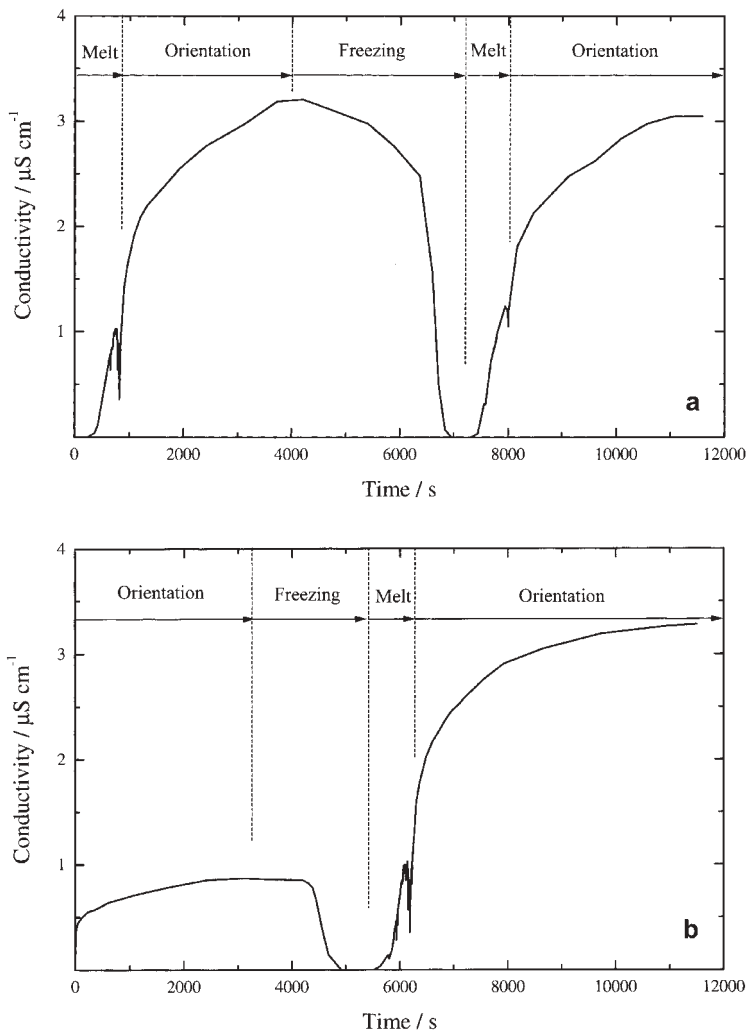
Figure 5. Electrical conductivity of PANI suspension (φ = 1%) in TCB during the freezing–melting (Melt) cycle and the orientation of PANI particles by the electric field in liquid suspension. The suspension was frozen (a) in the absence, and (b) in the presence of electric field. Electric field strength, E = 13 V mm^{-1}.

urethane network.[20] After PANI-TCB suspension has been melted again (Figure 5a), the original value of the conductivity is recovered.

When a fresh suspension is first placed in the electric field and PANI particles oriented, the electrical conductivity increases, but its limit value is more than 3 times lower (Figure 5b) than in the preceding case (Figure 5a).

This effect has been observed only when suspensions were frozen for the first time. After another freezing–melting cycle, the conductivity becomes considerably higher (Figure 5b). This observation might be explained by the changes in the morphology of the suspension. Potential aggregates of PANI particles present at the start (Figure 2) are penetrated by TCB. As TCB becomes solid, such conglomerates get broken into smaller objects by TCB crystals formed within them. The particle-size distribution of the conducting entities is thus changed and the resulting smaller particles become more efficiently organized in the electric field. The recovery of aggregates is prevented by the hydrophobization of the surface exposed during disaggregation to TCB.

Potential Application

A melting-point switch, a device that increases its conductivity by several orders of magnitude after its content has been melted and *vice versa*, could be constructed on the basis of PANI suspensions. The use of various liquids or their mixtures facilitates the setting of the melting point to the desired temperature. An isopycnic medium for the suspension is needed to prevent sedimentation of PANI particles. Such switches could be used in simple sensors or safety devices.

CONCLUSIONS

Polyaniline suspensions are a new class of liquid systems comprising electrically conducting polymers. Their electrical conductivity can be decreased by several orders of magnitude by freezing the suspension, while it is recovered after melting. Organization of PANI particles in the electric field is responsible for a larger electrical conductivity of the suspension in the liquid state.

REFERENCES

1. Y. Cao, J. Qiu, and P. Smith, *Synth. Met.* **69** (1995) 187–190.
2. J. Feng, A. G. MacDiarmid, and A. J. Epstein, *Synth. Met.* **84** (1997) 131–132.
3. M. Reghu, C. O. Yoon, C. Y. Yang, D. Moses, P. Smith, and A. J. Heeger, *Phys. Rev. B* **50** (1994) 13931–13941.
4. A. J. Heeger, *Trends Polym. Sci.* **3** (1995) 39–47.

5. J. Stejskal, P. Kratochvíl, and M. Helmstedt, *Langmuir* **12** (1996) 3389–3392.
6. D. Chattopadhyay and B. M. Mandal, *Langmuir* **12** (1996) 1585–1588.
7. S. Maeda, D. B. Cairns, and S. P. Armes, *Eur. Polym. J.* **33** (1997) 245–253 .
8. J. Stejskal, P. Kratochvíl, S. P. Armes, S. F. Lascelles, A. Riede, M. Helmstedt, J. Prokeš, and I. Křivka, *Macromolecules* **29** (1996) 6814–6819.
9. G. K. Elyashevich, A. G. Kozlov, N. Gospodinova, P. Mokreva, and L. Terle-mezyan, *Vysokomol. Soedin.* **B 39** (1997) 762.
10. L. G. B. Bremer, M. W. C. G. Verbong, M. A. M. Webers, and M. A. M. M. van Doorn, *Synth. Met.* **84** (1997) 355–356.
11. N. Kuramoto, M. Yamazaki, K. Nagai, K. Koyama, K. Tanaka, K. Yatsuzuka, and Y. Higashiyama, *Rheol. Acta* **34** (1995) 298–302.
12. N. Kuramoto, M. Yamazaki, K. Nagai, and K. Koyama, *Thin Solid Films* **239** (1994) 169–171.
13. C.-L. Huang, R. E. Partch, and E. Matijević, *J. Colloid Interface Sci.* **170** (1995) 275–283.
14. C. J. Gow and C. F. Zukoski, *J. Colloid Interface Sci.* **136** (1990) 175–188.
15. H.-Q. Xie, J.-G. Guan, and J.-S. Guo, *J. Appl. Polym. Sci.* **64** (1997) 1641–1647.
16. K. M. Blackwood and H. Block, *Trends Polym. Sci.* **1** (1993) 98–105.
17. D. C. Trivedi, in: H. S. Nalwa (Ed.), *Handbook of Organic Conductive Molecules and Polymers,* Vol. 2, Wiley, Chichester, 1997, pp. 505–572.
18. O. Quadrat and J. Stejskal, *J. Rheol.* **42** (1998) 13.
19. O. Quadrat, J. Stejskal, P. Kratochvíl, C. Klason, D. McQueen, J. Kubát, and P. Sáha, *Synth. Met.* **97** (1998) 37–42.
20. J. Stejskal, M. Špírková, O. Quadrat, and P. Kratochvíl, *Polym. Int.* **44** (1997) 283–287.
21. H. Scher and R. Zallen, *J. Chem. Phys.* **53** (1970) 3759–3761.
22. S. Kirkpatrick, *Rev. Mod. Phys.* **45** (1973) 574–588.
23. I. Balberg and N. Binenbaum, *Phys. Rev. B* **35** (1987) 8749–8752.
24. J. Prokeš, I. Křivka, and J. Stejskal, *Polym. Int.* **43** (1997) 117–125.
25. O. Quadrat, J. Stejskal, C. Klason, J. Kubát, and D.H. McQueen, *J. Phys.: Condens. Matter* **7** (1995) 3287–3294.
26. A. Lian, S. Besner, and L. H. Dao, *Mater. Lett.* **21** (1994) 215–219.
27. P. Banerjee and B. M. Mandal, *Macromolecules* **28** (1995) 3940–3943.
28. P. Banerjee and B. M. Mandal, *Synth. Met.* **74** (1995) 257–261.

SAŽETAK

Elekrična vodljivost suspenzije polianilina 2. Ciklus zaleđivanje–taljenje

Jakub Wojturski, Jaroslav Stejskal, Otakar Quadrat, Pavel Kratochvíl i Petr Sáha

Promjene električne vodljivosti suspenzije polianilina u 1,2,4-triklorbenzenu opažene tijekom zaleđivanja i taljenja medija objašnjene su promjenama u organizaciji vodljivih čestica u električnom polju pri različitim stanjima sustava. Vodljivost tekuće suspenzije za dva je reda veličine veća od vodljivosti zaleđene suspenzije.