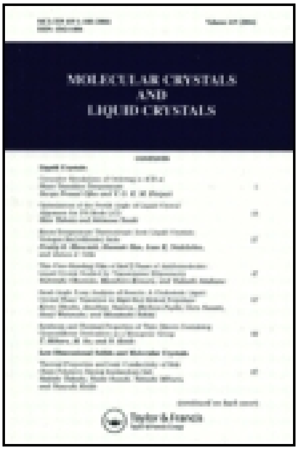

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

AC conductivity in aniline-1,4-phenylenediamine copolymers

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Version of record first published: 18 Oct 2010

To cite this article: O. Starykov, J. Prokeš, I. Křivka & J. Stejskal (2002): AC conductivity in aniline-1,4-phenylenediamine copolymers, Molecular Crystals and Liquid Crystals, 385:1, 33-42

To link to this article: http://dx.doi.org/10.1080/713738792

Mol. Cryst. Liq. Cryst., Vol. 385, pp. [153]/33–[162]/42
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1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290113042

AC CONDUCTIVITY IN ANILINE-1,4-PHENYLENEDIAMINE COPOLYMERS

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Copolymer samples were prepared by joint oxidation of aniline and 1,4-phenylenediamine with the possibility of controlling electrical properties by the changing of aniline content in the reaction mixture. Temperature dependence of DC conductivity, frequency dependence of AC conductivity and electric modulus were studied, with the aim to determine mechanisms of charge transport in the material. Due to low molecular weight, polyaniline and phenylenediamine units form amorphous material, similar to typical amorphous semiconductor, where doping leads to creation of electronic states which are localized in sites of dopant counterions. Charge transport takes place via variable range hopping (VRH) in 3 dimensions. The high disorder and broad distribution of relaxation times was found in these materials.

Keywords: conducting polymers; polyaniline; conductivity; dielectric relaxation; electric modulus; disorder

INTRODUCTION

Since the outstanding discovery of intrinsically conducting polymers, these attracted the interest of scientists [1–3]. Polyaniline has been proved to be useful for different applications [2,3]. Usually doping of polyaniline with organic or inorganic acids is used to create free or localized charges in a polymer medium. During this procedure the conductivity of polyaniline

This work is a part of the research program MSM113200002 that is financed by the Ministry of Education of the Czech Republic. The financial support of Grant Agency of Charles University (186/2001/B) is also gratefully acknowledged.

*Corresponding author. E-mail: starykov@karlov.mff.cuni.cz increases by several orders, from about 10^{-10} to 10^{1} S/cm [1–3]. The controlling of electrical properties of polyaniline is usually performed by change in doping level [4–5] or by mixing with non-conducting polymers [6,7]. The latter method allows create the materials with good mechanical properties, however, the conduction usually exhibits a percolation behavior. Another method for controlling the electrical properties of polyaniline is the copolymerization of aniline with monomers that produce non-conducting polymers [7]. Authors of [7] studied physical and electrical properties of copolymers made by joint copolymerization of aniline with three isomers of phenylenediamine. The poly(aniline-*co*-1,4-phenylenediamine)s were found to have almost linear semilogarithmic dependence of DC conductivity on aniline content in the reaction mixture. In the present article detailed analysis of conduction mechanisms taking place in these copolymers is made.

Several models were developed for the description of charge transport in conducting polymers [1]. Despite of high doping of polymer, the charge carriers seem to be localized, so they should move in the material by hopping over or tunneling through the potential barriers between the localized states. Variable range hopping (VRH) [8] is the most common charge transport mechanism, which assumes that carriers tunnel through the energy barriers between the localized states with help of phonon thermal energy. 3D-VRH occurs in the disordered polymers with structure similar to the amorphous semiconductors, where charges can choose a most easy hop in any direction. Quasi-1D VRH occurs in the polymers where charges move along the polymer chain, with sudden interchain hops [9]. In some cases polymerization and protonation leads to creation of small conducting islands distributing in non-conductive matrix. In such case charges tunnel between these regions according to charged energy limited tunneling (CELT) mechanism [10].

EXPERIMENTAL

Poly(aniline-*co*-1,4-phenylenediamine)s were prepared by joint oxidation of aniline hydrochloride and 1,4-phenylenediamine hydrochloride mixture using ammonium peroxodisulphate as oxidant. Samples were pressed into the pellets 13 mm in diameter. The AC and DC parameters were measured after vacuum deposition of gold electrodes, 10 mm in diameter, on both sides of pellets. The AC properties were measured in temperature range 100–320 K using precision LCR meters HP4284A and HP4285A in frequency range 20 Hz–5 MHz. Temperature and electric-field dependence of DC conductivity was measured using a Keithley 6517 electrometer in temperature range 100–320 K. The inner source of electrometer was used as the voltage source.

RESULTS AND DISCUSSION

The DC conductivity as a function of aniline content (molar fraction x) in the mixture with PDA for the set of poly(PANI-*co*-PDA) samples is shown on the Figure 1 (open squares). Conductivity of the copolymer changes in the range 10^{-9}–10^{0} S/cm with changing x from 10 to 90%. The approximate extrapolation of these results to 0 and 100% is in good agreement with the conductivity of PPDA and neat PANI (open circles on the Fig. 1). This paper concentrates on the detailed study of samples with aniline content on reaction mixture from 50 to 70%. Higher concentration of aniline produces the samples with high and frequency-independent conductivity that does not show any relaxation properties.

The temperature dependence of DC conductivity is shown in Figure 2 in a semilogarithmic scale. The narrow interval of measurement temperatures does not allow to precisely distinguish between the exponents $\frac{1}{2}$ or $\frac{1}{4}$ in equation describing VRH or CELT.

$$\sigma_{\mathrm{DC}} \propto \exp\left[-\left(\frac{T_0}{T}\right)^{\gamma}\right] \tag{1}$$

where γ should be $\frac{1}{2}$ for CELT and $\gamma = (d+1)^{-1}$ for VRH, where d is the dimensionality of a system. Among all, both above-mentioned models

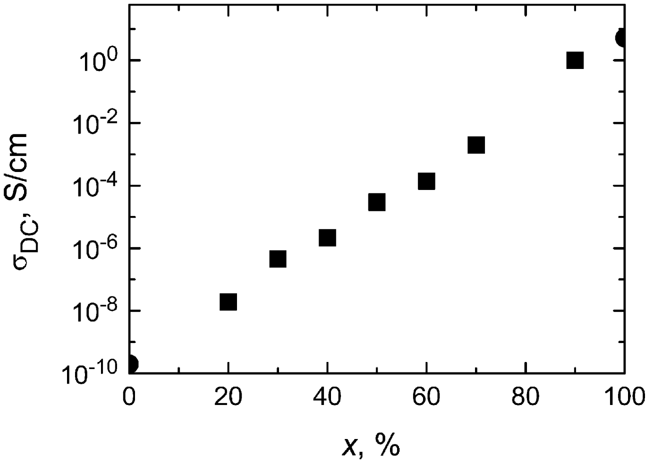

FIGURE 1 Dependence of copolymer DC conductivity on composition.

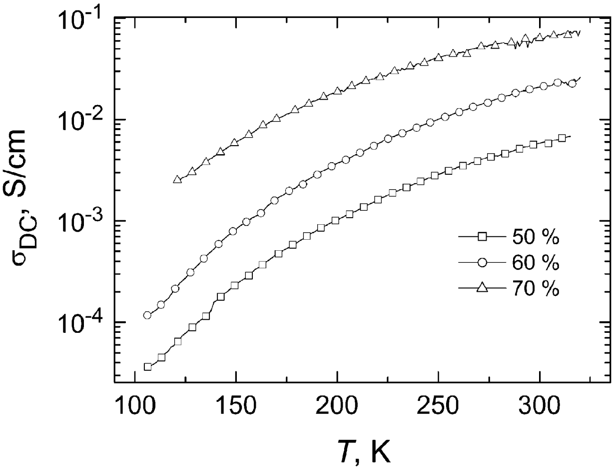

FIGURE 2 Temperature dependence of DC conductivity for samples with various compositions.

assume transition to Arrhenius behaviour towards higher temperatures (above 100 K).

The further investigations using the electric field dependence of DC conductivity has been made. Figure 3 shows the electric field dependence of DC conductivity measured on the sample with 50% of aniline at room temperature. The best fit is obtained with use of equation

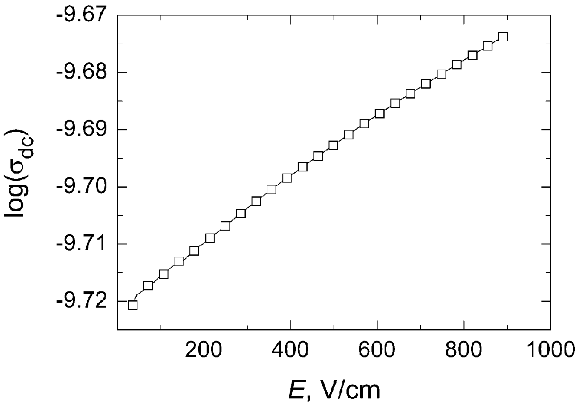

FIGURE 3 Electric field dependence of conductivity for the sample with $x = 50$ at room temperature.

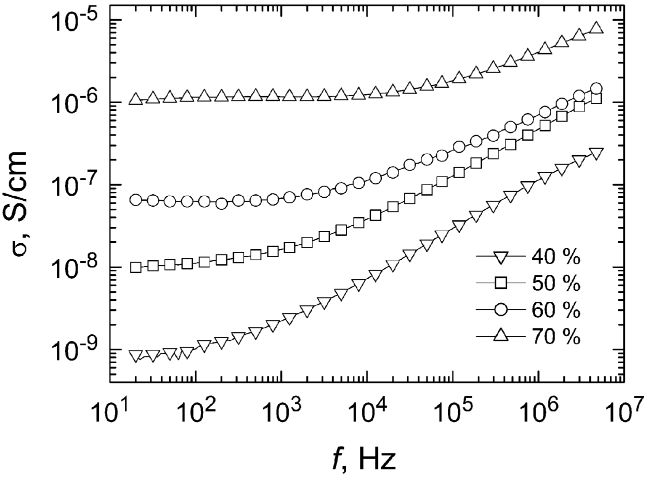

FIGURE 4 Frequency dependence of AC conductivity for samples with various compositions.

$$\sigma_{\mathrm{DC}} \propto \exp\left(\frac{eRE}{k_{\mathrm{B}}T}\right) \tag{2}$$

which corresponds to the VRH mechanism. Value of mean hopping distance calculated from this fit was about 10 nm, which is in a good agreement with results of other studies [11].

Figure 4 shows the frequency dependence of total conductivity, $\sigma(\omega)$ measured at 130 K for the samples made with aniline content from 40 to 70%. The low-frequency limit of $\sigma(\omega)$ increases with increasing x with simultaneous increase in characteristic, or onset frequency ω_c. Below this frequency, the conductivity is almost constant, and beyond it increases with frequency. So, one may conclude that samples with high x will behave like metal concerning the behavior of $\sigma(\omega)$, so their conductivity tends to be frequency-independent.

The effect of temperature on the sample with 50% of aniline is shown in Figure 5. The influence of temperature is similar to that of sample composition, since low-frequency limit of total conductivity, σ_0 and ω_c increase with temperature. Frequency ω_c changes from about 100 at 100 K to $\sim 10^6$ at 200 K. DC conductivity increases from $\sim 10^{-9}$ at 100 K to $\sim 2 \times 10^{-6}$ at 200 K. The approximate power law of AC conductivity $\sigma(\omega) \sim \omega^s$ [8] holds above ω_c with an exponent s about 0.6. At the high temperatures conductivity tends to be more independent on frequency.

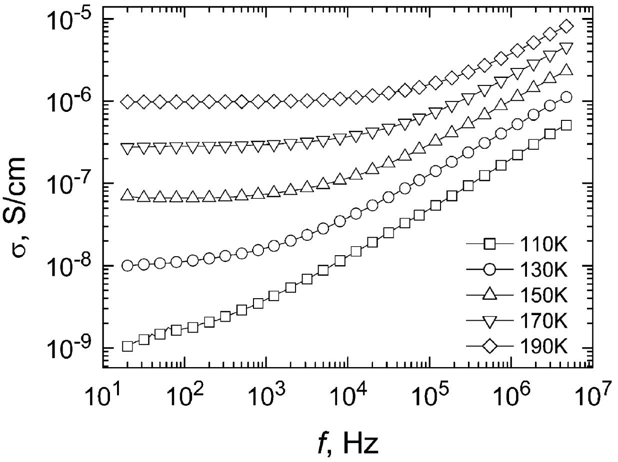

FIGURE 5 Frequency dependence of AC conductivity of the sample with 50% aniline for the set of temperatures.

The total frequency-dependent conductivity of the conducting material can be described as

$$\sigma(\omega) = \sigma_{\mathrm{AC}}(\omega) + \sigma_{\mathrm{DC}} \tag{3}$$

where

$$\sigma_{\mathrm{AC}}(\omega) \propto \omega \ln^{d+1}\left(\frac{\nu_{\mathrm{ph}}}{\omega}\right) \sim \omega^{s} \tag{4}$$

is the AC conductivity, ω is the angular frequency and ν_{ph} is the phonon attempt frequency. Curves showed in Figure 4 were fitted to the Eq. (4). The values of ν_{ph} obtained from the equations for 3D VRH ($\sim 10^{11}\,\mathrm{s}^{-1}$) are closer to generally accepted value known from literature ($\sim 10^{13}$) [8], whereas quasi-1D VRH approach gives too low values ($\sim 10^{8}\,\mathrm{s}^{-1}$). It indicates that the 3D VRH takes place in these materials.

Due to high DC conductivity of particular materials, representation of AC measurements in terms of dielectric permittivity is impossible, because the peak in ε'' is masked by the contribution from DC conductivity [12]. It were found that in particular case of materials which normally have freely moving charges it is convenient to present the results of AC measurements in terms of complex conductivity or complex modulus, which is the quantity reciprocal to complex permittivity $M^{*}(\omega) = 1/\varepsilon^{*}$. This quantity represents a Fourier transform [13]

$$M^{*}(\omega) = M_{\infty}\left[1 - \int_{0}^{\infty}\left(-\frac{d\varphi(t)}{dt}\right)\exp(-i\omega t)dt\right] \tag{5}$$

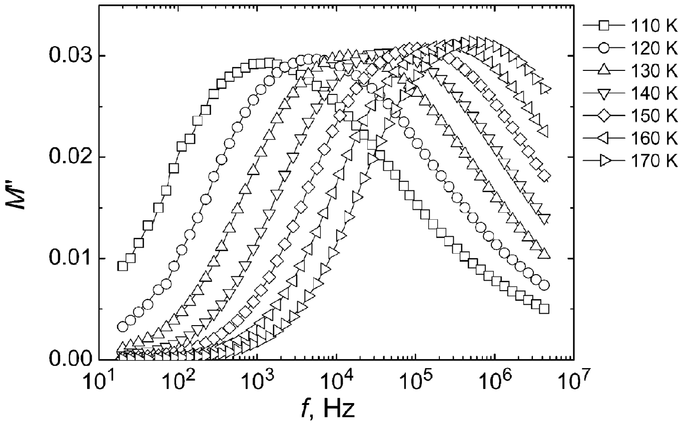

FIGURE 6 Frequency dependence of electric modulus measured on the sample with 50% of aniline for the set of temperatures.

of the decay function of electric field $\varphi(t)$, which in most cases can be presented in the form of Kolhrausch-Williams-Watts (KWW) function

$$\varphi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right]. \tag{6}$$

Figure 6 shows the frequency dependence of electric modulus of the sample with $x = 50\%$ measured at the temperatures from 110 to 200 K. The shape of curves and magnitude of maximum do not change with temperature.

Figure 7 shows the results of fitting of Eq. (5) to the experimentally obtained curves of electric modulus for the sample with 50% aniline at 130 K. The best fit was found for $\beta = 0.32$. Since the shape of modulus curve remains the same with changing temperature (Fig. 6), it gives the possibility to construct the master curve, and one can note that β is temperature independent.

The mean relaxation time τ_0, obtained from the fitting of experimentally measured values and converted to relaxation frequency $\omega_0 = 1/\tau_0$, is shown in Figure 8 as an Arrhenius plot $\ln \omega_0 = \ln \nu_{\mathrm{ph}} - \frac{W}{kT}$. Table 1 summarizes values of phonon attempt frequency ν_{ph} and activation energy W calculated from linear fitting of these plots to the Arrhenius equation. For the comparison, the last column contains the values of ν_{ph} obtained from the fit of AC conductivity curves to the 3D-VRH model.

Parameter β characterizes polymer structure and depends on the polymerization conditions, which can be slightly different even for the same composition (fluctuations in space distribution of monomers during

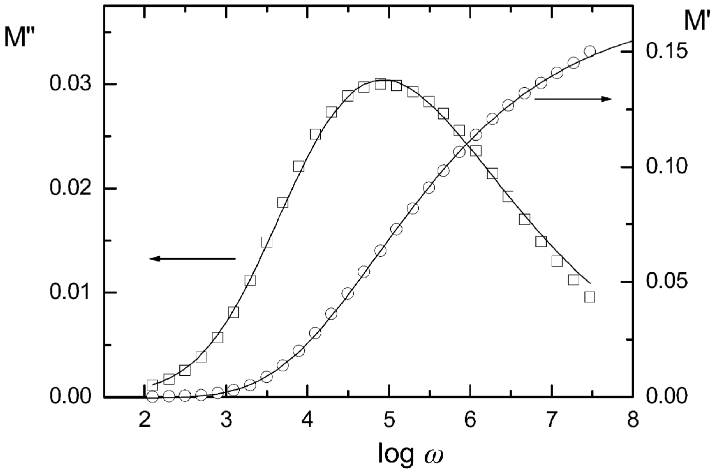

FIGURE 7 Results of fitting of experimental data to the KWW function.

polymerization, etc). This parameter does not correlate with composition of sample. Otherwise, activation energy W depends on the number of localized states and decreases with growing content of aniline (which represents conducting component). The values of ν_{ph} obtained from the Arrhenius plots are in a good agreement with those calculated from the fit of experimental plots of AC conductivity to the 3D hopping model, Eq. (4).

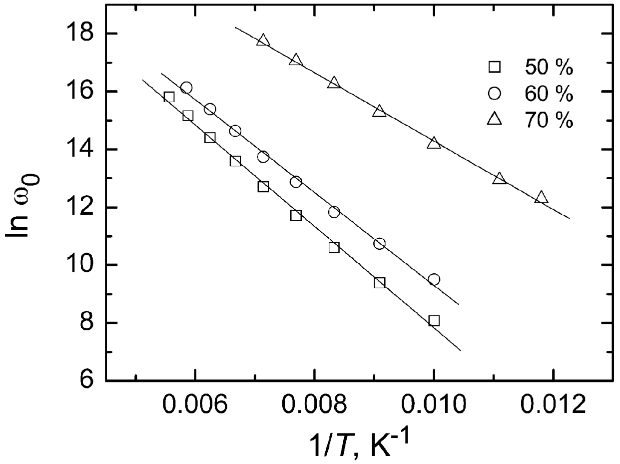

FIGURE 8 Temperature dependence of relaxation frequency, plotted in the form of Arrhenius plot.

TABLE 1 Fit Parameters for Copolymer Samples

Aniline content, %	β	ν_{ph} (Arrh.), s^{-1}	W, eV	ν_{ph} (AC Cond.), s^{-1}
50	0.32	$1.05\ 10^{11}$	0.15	$1.17\ 10^{11}$
60	0.41	$6.4\ 10^{10}$	0.13	$5.4\ 10^{10}$
70	0.36	$2.17\ 10^{11}$	0.1	$4.25\ 10^{11}$

CONCLUSIONS

Changing of copolymer composition is an effective and economic method of controlling its electrical properties. Increasing aniline content from 0 to 100% leads to increase in DC conductivity by 10 orders of magnitude. The measurements of temperature and electric field dependence of DC conductivity showed that charge transport does not correspond to CELT mechanism, indicating that the copolymerization yields the number of localized states in material, rather than highly conducting regions dispersed in non-conducting matrix. Frequency dependence of AC conductivity is a typical one for hopping conductivity; the onset frequency and activation energy increases with growing aniline content. The value of phonon frequency implies that the hopping charges move according to 3D-VRH rather than to quasi-1D. It is probably due to high inhomogeneity in monomer distribution during the copolymerization. The disorder is confirmed by the wide distribution of relaxation times, corresponding to low value of stretch parameter β in distribution function.

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