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EPR and ESEEM Identification of Free Radicals and Molecular Structure of the Oligomers Formed During Polycondensation of 1-Chloro-4-nitrobenzene with Sodium Sulfides in N-Methyl-2-pyrrolidone

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The synthesis of derivative of poly (4-hydrazo-diphenylenedisulfide) by reaction of 1-chloro-4-nitrobenzene with sodium sulfide and disulfide in N-methyl-2-pyrrolidone leads to oligomeric products with average molecular weight of the homogeneous chains 1182 g/mol and 690 g/mol, respectively. The mechanisms of the reactive intermediates polycondensation reaction are described. The products were characterized by IR, ^{1}H NMR, and EPR spectroscopy and by elemental analysis. The final amorphous oligomer products contain mostly diamagnetic species and about 1% of paramagnetic species. The latter produce strong isotropic EPR signal at $g = 2.0025$ from free radical with concentration of about 10^{18} radicals/gram. Pulsed EPR spectroscopy allowed identifying the radical by analysis of the electron spin echo envelope modulation spectrum. The radical is localized on the carbon atom of the C=O-group of the N-methyl-2-pyrrolidone moiety with broken internal C–N bond of the lactam ring.

Key words: poly (4-hydrazo-diphenylenedisulfide), oligomers, radical polymerization, radical EPR, ESEEM

Poly (1,4-phenylene sulfides) are oligomeric materials with excellent plastic performance of commercial interest. They form durable insulating coatings and are cementing agents. The products of medium molecular weight, containing oligomers up to octamers, are formed by the reaction of sulfur or sodium sulfide with *para*-substituted chlorobenzenes [1,2]. The reaction is not a simple stepwise polycondensation. $HS^{\bullet}$ formed in a one-electron transfer process initiates the chain formation and the reaction goes with reactive intermediate radicals and radical cations. This reaction can be called the reactive intermediate polycondensation. The reaction temperature must be higher than 150°C to cleave the disulfide linkage homolytically allowing surviving the chain forming carriers.

In this paper we report synthesis of poly (4-hydrazo-diphenylenedisulfide) by a reaction of 1-chloro-4-nitrobenzene (PCNB) with sodium sulfide and disulfide in a polar solvent N-methyl-2-pyrrolidone (NMP) at high temperatures. The reaction carried out in this solvent gives the highest reaction rate and leads to products with relatively high molecular weight. An activation of N-methyl-2-pyrrolidone molecule to a radical form by a transfer of electron from HS^- allows bonding this molecule to the end of forming chains. It is well known that polymerization of the lactams is a ring-opening process [3] and the linkage is formed usually *via* carbon atom of the C=O group. In this paper we will show that the linkage at CH_2-group of pyrrolidone ring is formed with simultaneous ring opening. It is preferred by amine groups bonded to aromatic ring at the end of the polymer chains.

During the gelation of a reaction mixture or the transition to the glass state, after homogeneous chain polycondensation proceeded *via* free radical or radical ion mechanisms, the radicals can be trapped in stable positions with concentration high enough to be detected by EPR [4]. Radical recombination in a solidified mass of polymeric material can be a very slow process and the radicals can be stable at room temperature over a period of months, especially for high molecular mass or highly cross-linked polymers. Usually the EPR spectrum in solid or highly viscous polymeric materials consists of a single symmetrical or asymmetrical line. The lack of resolved hyperfine structure makes difficult to identify radical uniquely. Such situation we have found in the final oligomer product of our system, which displayed a strong structureless electron paramagnetic resonance (EPR) signal. In this paper we describe the steps of the polycondesation reaction and characterize its product with an identification of the free radical formed during the reaction using EPR and electron spin echo envelope modulation (ESEEM) spectroscopy. The latter technique uses a pulse excitation of EPR lines and the Fourier transform of the decay of electron spin echo amplitude. This gives an ENDOR-type spectrum with lines allowing identifying the magnetic nuclei surrounding the radical center, thus clearing up its molecular and geometrical structure.

EXPERIMENTAL

Materials: 1-Methyl-2-pyrrolidone (NMP) was purified by vacuum distillation and stored over 4-Å molecular sieves. 1-Chloro-4-nitrobenzene (PCNB) (Aldrich) was purified by recrystallization from methanol. Sodium disulfide was prepared from sodium sulfide (Aldrich) and sulfur in ethanol at the reflux temperature. DMSO and DMF were purified by the usual method.

Polycondensation: Polycondensation of PCNB with sodium sulfide and disulfide was carried out in a polar medium (N-methyl-2-pyrrolidone) for sake of the good solubility of substrates and products as well as to have the high process effectiveness. In the reaction of PCNB with sodium sulfide and disulfide in NMP at 170–200°C for about 15 h under argon oligomeric products were obtained and then heated in argon atmosphere.

The reaction of 1-chloro-4-nitrobenzene with sodium sulfide (PCNB+Na_2S) was carried out as follows. A solution of 48 g (0.2 mole) of $Na_2S \cdot 9H_2O$ in 100 cm^3 of N-methyl-2-pyrrolidone was placed in a three-necked flask equipped with a stirrer, thermometer and condenser. It was heated in an atmosphere of argon to the complete removal of the crystallization water. A solution of 31.6 g (0.2 mole) of 1-chloro-4-nitrobenzene in 50 cm^3 of N-methyl-2-pyrrolidone was heated to 150°C and introduced into the flask. Polycondensation was then carried out under reflux at 200°C for 15 h under argon. The reaction mixture was poured into 500 cm^3 of distilled water and the precipitate was filtered, washed with hot absolute ethanol and dried in air. This product was obtained in 59% overall yield; the reduced viscosity was 0.19 $dL \cdot g^{-1}$ in DMSO. M/z: 1182 g/mol. IR (KBr) ν (cm^{-1}): 3450 (N–H, st), 1702 (C=O, st), 825 (1,4-aromatic substitution, st), 746, 528 (C_{arom}–S-, m). ^{1}H NMR [300, MHz, $(CD_3)SO$, δ ppm]: 7.2 (m, Ar, 8H), 6.6 (s, NH, 1H), 5.5 (s, NH, 1H), 2.1 (s, CH, 2H), 1.1 (s, CH, 2H). Elem. anal.: Calcd. for $C_{58}H_{56}S_8N_{10}O_2$: C, 58.57%; H, 4.99%; N, 11.93%. Found: C, 58.88%; H, 4.91%; N, 11.84%.

The reaction of 1-chloro-4-nitrobenzene with sodium disulfide (PCNB+Na_2S_2) was carried out as follows: A solution of sodium disulfide, prepared by dissolving 3.2 g (0.1 mole) of sulfur in a solution of 24 g (0.1 mole) of sodium sulfide in 50 cm^3 of hot absolute ethanol, was added to 31.6 g (0.2 mole) of 1-chloro-4-nitrobenzene in 150 cm^3 of NMP. In the first stage bis-(p-nitro phenyl) disulfide was obtained; yellow crystals (69 % yield); m.p.: 168–170°C; IR (KBr) ν (cm^{-1}): 1530, 1340 (–NO_2, st), 840 (1,4–aromatic substitution, st), 745, 466 ($C_{arom.}$–S-, st). Elem. anal. Calcd. for $C_{12}H_8S_2N_2O_4$: C, 46.85%; H, 2.53%; N, 9.42%. Found: C, H, 2.60%; N, 9.02%.

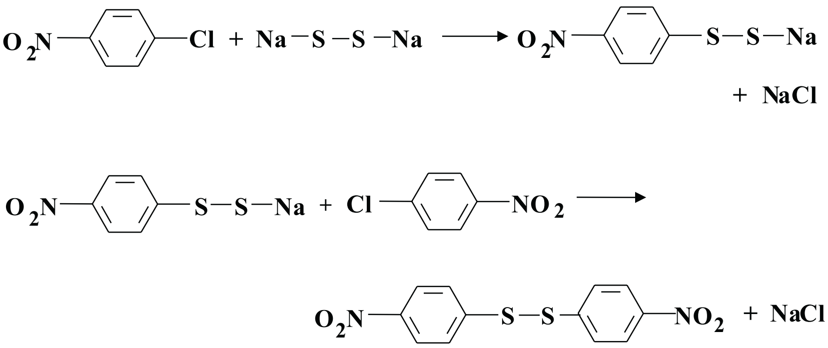
The mixture was heated under reflux at 170°C and 200°C for 15 h under argon. The next steps were carried out similarly to the PCNB+Na_2S procedure. The product was obtained in 46% overall yield (**2b**); the reduced viscosity was 0.12 dL·g^{-1} in DMSO. M/z: 690 g/mol. IR (KBr) ν (cm^{-1}): 3350 (N–H, st), 1710 (C=O, st), 825 (1,4-aromatic substitution, st), 740, 516 (C_{arom}–S-, m). ^{1}H NMR [300, MHz, $(CD_3)SO$, δ, ppm]: 6.7–8.1 (m, Ar, 8H), 6.6 (s, NH, 1H), 5.5 (s, NH, 1H), 2.1 (s, CH, 2H), 1.1 (s, CH, 2H). Elem. anal.: Calcd. for $C_{34}H_{36}S_4N_6O_2$: C, 59.00%; H, 5.38%; N, 12.23%. Found: C, 59.13%; H, 5.51%; N, 12.17%; and 64% yield (**2c**); the reduce viscosity was 0.26 dL·g^{-1} in DMSO. IR (KBr) ν (cm^{-1}): 3351 (N–H, st), 1707 (C=O, st), 824 (1,4-aromatic substitution, st), 743, 522 (C_{arom}–S-, m). ^{1}H NMR [300, MHz, $(CD_3)SO$, δ, ppm]: 7.6 (m, Ar, 8H), 6.5 (s, NH, 1H), 5.4 (s, NH, 1H), 2.1 (s, CH, 2H), 1.1 (s, CH, 2H). Elem. Anal.: Calcd. for $C_{34}H_{36}S_4N_6O_2$: C, 59.0%; H, 5.3%; N, 12.23%. Found: C, 59.1%; H, 5.51%; N, 12.17%.

Physical measurements: NMR spectra of ^{1}H were recorded on a Varian spectrometer (300 MHz) using $(CD_3)_2SO$ as a solvent. The spectra were relatively weak because of the line broadening due to interaction with paramagnetic radical centers. Mass spectra (MS) were recorded on MASPEC – AMD 402 and AMD 604 spectrometers and the M/z values were obtained from distribution of the molecular weights. IR spectra were recorded on a FT–IR Bruker (IFS 113 ν) spectrophotometer in KBr. The melting point was determined by the DSC method, which was performed on a Netzsch DSC 200. The reduced viscosity was measured in a solution of 0.6 g in 100 cm^3 of dimethyl sulfoxide at 25°C. Continuous-wave EPR spectra were recorded at 293 K and at 77 K on a Radiopan SE/X-2547 spectrometer operating at X-band microwave frequencies with a rectangular TE_{102} cavity and 100 KHz magnetic modulation. The EPR lines displayed no saturation effects both at room and liquid nitrogen temperature and were recorded with 7 mW microwave power and 0.125 mT modulation. The g-factors describing the EPR line positions in the magnetic field were calculated as $g = 71.4484\,\nu/B$, where ν is the resonance frequency (in GHz) measured by HP 5340A frequency counter, and B is the magnetic field (in mT) determined from field markers generated by the NMR magnetometer. Number of spins in the samples was determined by EPR with respect to the Ultramarine Blue Standard sample having 6×10^{15} spins of the $\dot{S}_3$ radicals. The standard sample EPR signal consists of a single Lorentzian line at $g = 2.029$ with peak-to peak line width $\Delta B_{pp} = 1.90$ mT. Pulsed EPR experiments were performed on a Bruker ESP 380E FT/CW spectrometer at 9.7 GHz in the temperature range 4.2–300 K using Oxford CF935 flow helium cryostat. Electron spin echo of the Hahn-type was generated by two 48 ns pulses having 0.74 mT spectral width, with initial time interval τ = 200 ns. The electron spin echo (ESE) decay was weakly modulated by dipolar interaction of the radical center with surrounding magnetic nuclei. These modulations were studied in details using three pulse sequences 48 ns–τ–48 ns–T–48 ns–echo with τ =200 ns interval and 8 ns incremented T-interval. The stimulated echo generated by the three pulses was recorded, whereas the other unwanted echoes were smeared out by phase cycling of pulses using a standard Bruker spectrometer routine. The Fourier transform of the modulation function was applied to obtain an ENDOR-type spectrum.

RESULTS AND DISCUSSION

Mechanisms of the polycondensation and its product: The first stage of reactions of 1-chloro-4-nitrobenzene with sodium sulfide or disulfide in N-methyl-2-pyrrolidone is a substitution of sulfur for chlorine [5,6] (Scheme 1). In this stage the bis(p-nitrophenyl) disulfide was obtained. In the second stage there is a progressive reduction of nitro groups (Scheme 2) in agreement with the data of Montanari *et al.* [7]. Based on ^{1}H NMR, IR, MS spectra and elemental analyses we have proved that the product is poly (4-hydrazo-diphenylenedisulfide) (**1**), which contained the disulfide and hydrazo groups between phenyl rings.

Scheme 1

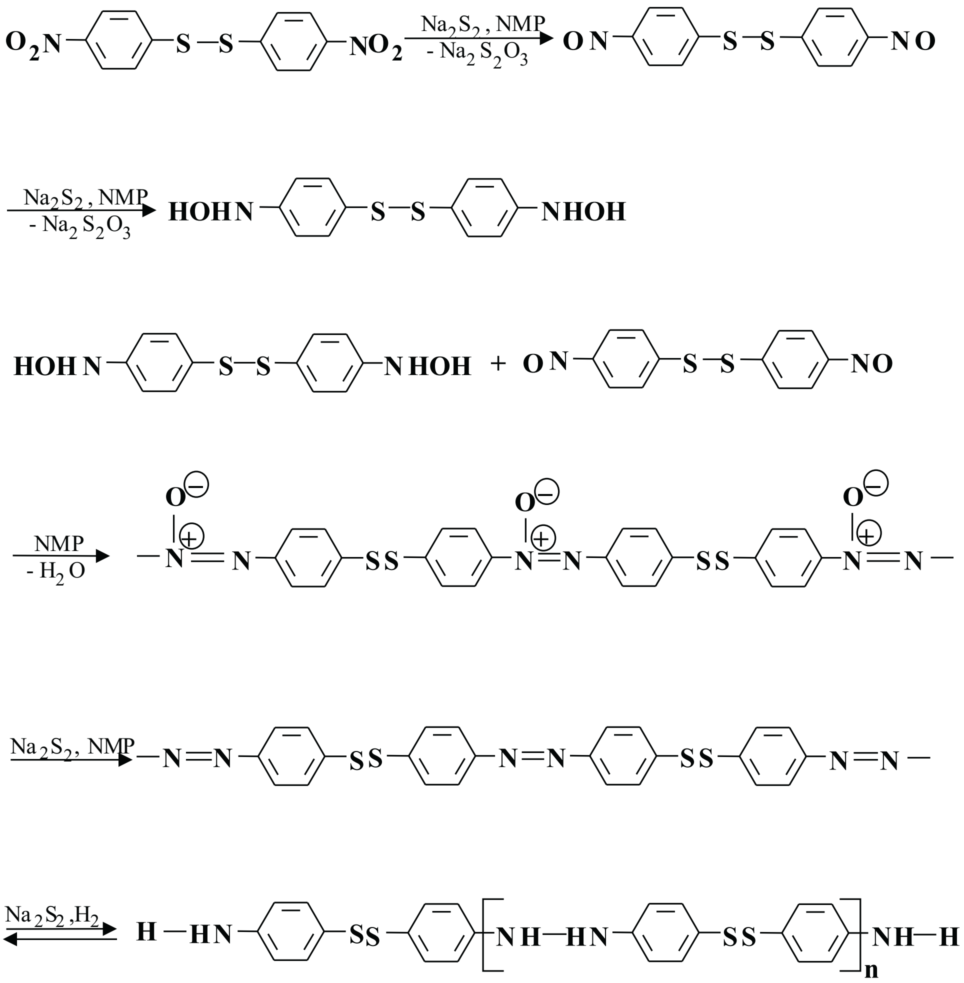


Above 160 C these oligomers reacted with N-methyl-2-pyrrolidone according to the mechanism described in [8]. Transfer of electron from NaS^{-} to NMP molecule (Scheme 3) allows a reaction with terminal amine group of the poly (4-hydrazo-diphenylenedisulfide) chain. The lactam molecules are deprotonated with 4-hydrazo-diphenylenedisulfide (Scheme 4) as observed in similar systems [9,10]. The resulting oligomers with NMP chain-ends can be diamagnetic or paramagnetic as shown by EPR data discussed below. The proposed forms of the chain-end are shown in Scheme 4 as left (diamagnetic) and right (paramagnetic) sides, respectively, and will be discussed below.

The final oligomeric products (**2**) of high reduced viscosity (in DMSO) were obtained as a black amorphous powder. The products were soluble in aprotic polar solvents such as N-methyl-2-pyrrolidone, N,N-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). Their oligomeric character being confirmed by the value of the reduced viscosity, namely: 0.19 dL· g^{-1} (PCNB, Na_2S, 200 C) (**2a**), 0.12 dL·g^{-1} (PCNB, Na_2S_2, 170 C) (**2b**), 0.26 dL· g^{-1} (PCNB, Na_2S_2, 200°C) (**2c**). All the oligomers show no the melting point in DSC but only endothermic transitions above 220 C.

The IR spectra of oligomers are very similar. The spectrum of **2b** is shown in Figure 1. The spectra reveal bands at 825 cm^{-1} due to a 1,4-disubstituted benzene ring. The strong absorption due to N–H is observed at 3350 cm^{-1}. In the spectra there are bands at around 740 cm^{-1} and 516 cm^{-1} characteristic of the diphenyl disulfide. The strong bands at 1710 cm^{-1} correspond to the carbonyl group.

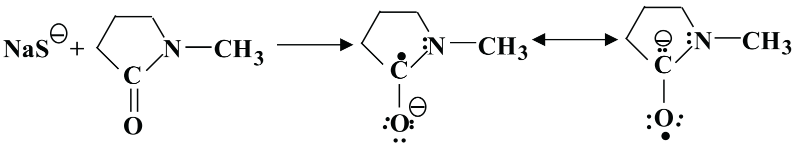
Scheme 2



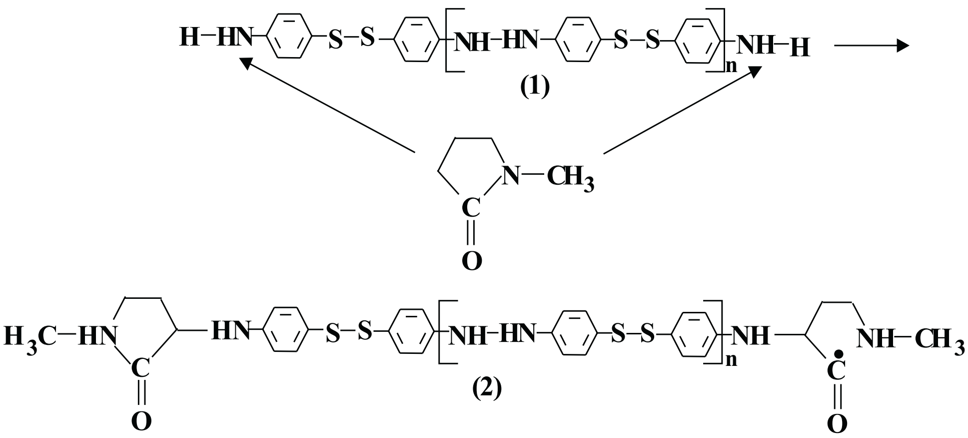
(1)

A few bands are observed in ^{1}H NMR spectrum of **2b** (Figure 2): an aromatic multiplet around 7.2 ppm (8H), singlets at: 6.6 ppm (1H), 5.5 ppm (1H) and 8.1 ppm (1H) characteristic of the protons of N–H groups, and two aliphatic singlets at 2.1 ppm (2H) and 1.1 (2H). The relative band intensity confirms proposed molecular structure of oligomer **2b** with predominating dimeric species for which the following ratio of protons is expected as: aromatic/NH = 8/3, aromatic/aliphatic = 2.

Scheme 3



Scheme 4



2a: n = 2-3 (PCNB, Na_2S)
2b: n = 1-2 (PCNB, Na_2S_2, 170℃)
2c: n = 2-4 (PCNB, Na_2S_2, 200°C)

EPR spectra and radical concentration: The electron paramagnetic resonance (EPR) spectroscopy is known as a useful method for free radical detection, determination of their electronic structure and evaluation of the radical concentration. Five samples we have studied by EPR: (**I**) – PCNB+Na_2S (**2a**) with reaction performed at 200 C; (**II**) – PCNB+Na_2S_2 (**2b**) with reaction at 170 C; (**III**) – PCNB+Na_2S_2 (**2c**) with reaction at 200 C; (**IV**) – PCNB+Na_2S_2 (**2b**) (170) purified and then annealed at 350°C in air; (**V**) – PCNB+Na_2S_2 (**2b**) (170) no purified and annealed at 350 C in air. Samples of **I–III** were in form of a black powder, whereas the annealed samples **IV** and **V** were in form of sintered glassy-like solids. EPR spectra consist of a single resonance line. The line is symmetrical and very close to the Lorentzian shape for samples **I–III**, which were not thermally annealed, as is shown in Fig. 3a for the sam-

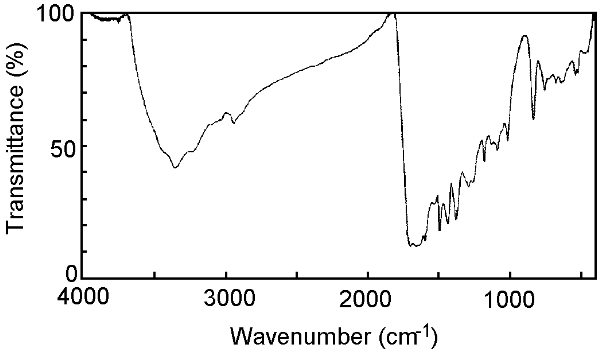


Figure 1. FTIR spectrum of **2b** (PCNB+Na$_2$S$_2$, 170°C).

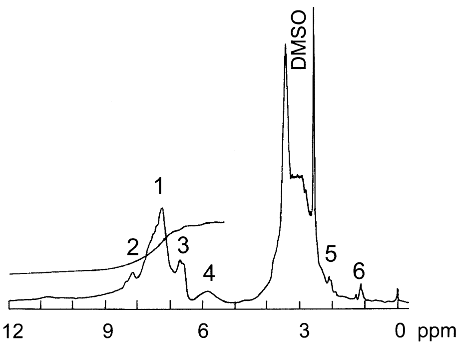


Figure 2. NMR spectrum of **2b** (PCNB+Na$_2$S$_2$) in DMSO. The lines are broadened due to short relaxation time resulting from coupling to the paramagnetic radicals. The DMSO solvent peak dominates. Other peaks are: 1– aromatic protons; 2 – NH-groups of pyrrolidone; 3 – NH-groups bridging chain and pyrrolidone molecules; 4 – NH-groups of the chain; 5 – CH$_2$-groups of pyrrolidone; 6 – terminal CH$_3$ groups.

ple **II** (**2b**). The annealed samples display slightly asymmetrical EPR (Fig. 3c). An asymmetry of EPR lines appears also in spectra recorded at 77 K as shown for PCNB+Na$_2$S (sample **I**, **2a**) in Fig. 3b. The EPR parameters and number of spins per gram for the five samples are summarized in Table 1. As can be seen from Fig. 3, except the main EPR signal there exists a weak EPR line in all samples. This narrow line with $\Delta B_{pp} = 0.07$ mT is positioned at higher magnetic field with $g = 1.9990$. It is an intrinsic signal produced by an unidentified radical center, most probably related to highly delocalized unpaired electrons or even itinerant electrons in the samples.

The g-factors, characterizing the effective magnetic moment of the unpaired electron, are close to the free spin values $g_e = 2.0023$ characteristic for radicals localized on an atom with low spin-orbit coupling, like nitrogen or carbon. The location of the radical on the carbon atom of the N-methyl-2-pyrrolidone moiety is strongly sug-

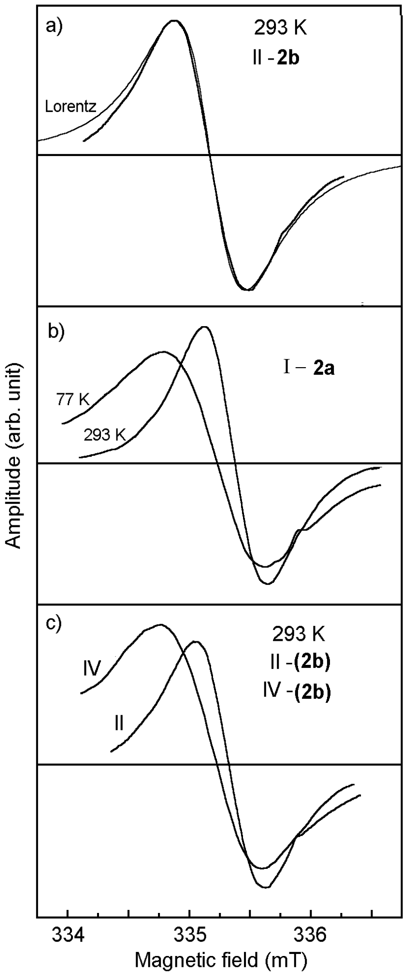


Figure 3. EPR spectra recorded at 9.4 GHz: a) Sample II: PCNB+Na_2S_2 (**2b**) and its approximation by the Lorentzian line; b) Sample I: PCNB+Na_2S (**2a**) recorded at room and liquid nitrogen temperature; c) Comparison of room temperature EPR lines of PCNB+Na_2S_2 (**2b**) in powder sample II and in annealed glassy sample IV.

gested by practically isotropic *g*-factor and symmetrical EPR line of our samples. The carbon centered cation-radical was found in UV-irradiated polyvinyl acetate with isotropic $g = 2.0032$ and structureless EPR line [11]. Nitrogen-centered radical can be excluded since $^{14}N(I=1)$ nucleus is magnetic and thus the hyperfine triplet with anisotropic splitting order of 1.5 mT should be observed instead of the single line [12]. Relatively narrow resonance lines, order of 0.6 mT and the absence of the hyperfine splitting clearly indicate that the radical is localized on a carbon atom not bonded to nitrogen or CH_2-group, which confirm our conclusion that NMP- molecules are linked to oligomeric chains by CH_2-groups as is shown in Scheme 4.

Table 1. Radical concentration and EPR parameters.

Sample	Radical concentration c_r	Number of chains[a] per single radical n	EPR parameters[b]	
			295 K	77 K
I = (**2a**) PCNB+Na_2S	9.2(±3.0) 10^{18}/gram	55	g = 2.0023 ΔB_{pp} = 0.53 mT symmetrical line	g = 2.0032 ΔB_{pp} = 0.80 mT asymmetrical line
II, **III** = (**2b**), (**2c**) PCNB+Na_2S_2	3.8(±1.0)·10^{18}/gram	230	g = 2.0025 ΔB_{pp} = 0.59 mT symmetrical line	g = 2.0025 ΔB_{pp} = 0.59 mT symmetrical line
IV = (**2b**) PCNB+Na_2S_2 purified, annealed	2.1(±0.5)·10^{18}/gram	415	g = 2.0031 ΔB_{pp} = 0.87 mT asymmetrical line	g = 2.0025 ΔB_{pp} = 0.73 mT symmetrical line
V = (**2b**) PCNB+Na_2S_2 unpurified, annealed	1.0(±0.5)·10^{18}/gram	870	g = 2.0024 ΔB_{pp} = 0.63 mT slightly asymmetrical line	g = 2.0029 ΔB_{pp} = 0.42 mT asymmetrical line

[a] $n = N_A/(m_c c_r)$ with average molecular weight of the polymer chain (determined from MS): m_c = 1182 g/mol for sample **I** (**2a**), and m_c = 690 g/mol for sample **II** (**2b**).

[b] Errors: g-factor: ± 0.0003; peak-to-peak line width ΔB_{pp}: ± 0.02 mT. The g-factors for asymmetrical line were determined from the magnetic field value at zero level of the line.

The fresh samples and purified samples annealed at 350 C in air show small changes in EPR spectra (Fig. 3c) typical for oxidation of polymers. Broadening and asymmetry of the lines indicate the appearance of new radical centers, due to the penetration of a solidified polymer by the oxygen. Solid sample EPR spectra recorded at 77 K are not very informative and show only some small transformations expected, when the EPR line is multi-component or when molecular dynamics is hindered at low temperatures. The number of radicals is much lower than the number of chains in the solidified polymer. This suggests that the final products of the polycondensation reaction exist mostly in the neutral form and only about 1% exists in the stable radical form. The molecular structure of both forms is discussed in the next section.

Electron spin echo signal and ESEEM spectra: The electron spin echo (ESE) signal was observed in the whole temperature range (4.2–300 K), for all studied samples, indicating that the EPR lines are inhomogeneously broadened, *i.e.* are formed from "spin-packets" being non-resolved hyperfine lines. From the ESE decay time (phase memory time T_M) the line width of the spin-packets can be evaluated as 0.02 mT. So, the observed structureless EPR lines are in fact formed by a few tenth of hyperfine lines resulting from the weak dipolar interaction of the radical with surrounding magnetic nuclei.

Additional information can be obtained from Fourier transform ESE spectroscopy (ESEEM spectroscopy), which delivers information about the surrounding magnetic nuclei. The two-pulse ESE amplitude decreases with time after excitation, *i.e.* depends on the interpulse interval. This decrease can be produced by various mechanisms, one of which is the dipolar coupling between the unpaired electrons and surrounding magnetic nuclei. This weak interaction produces, moreover, the oscillations of the ESE amplitude decay, which are termed the Electron Spin Echo Envelope Modulation (ESEEM). The oscillation frequencies are equal to the precession motion frequencies of the nuclear magnetic moments (Larmor nuclear frequencies). The Fourier transform of the ESE modulation function gives an ESEEM spectrum (FT-ESE spectrum), which display peaks at modulation frequencies as in ENDOR spectra, and allows identifying the surrounding nuclei [13]. The atoms involved directly in the chemical bonding with radical-center produce splitting of EPR line (resolved hyperfine structure) and do not contribute to ESEEM.

The ESE decay of the radical in our polymeric systems displays relatively weak modulation effect. This is shown in Fig. 4, where modulated ESE decay of the three pulses stimulated echo and it Fourier transforms spectrum are shown. We have recorded the stimulated echo signal instead of two-pulse echo since the three-pulse ESEEM is simpler and do not contain combination peaks of the fundamental nuclear frequencies.

The peaks in the FT spectrum arise from interaction with surrounding protons and nitrogen nuclei having the following nuclear parameters: ^{1}H: I = ½, ν_H = 14.2805 MHz; ^{14}N: I = 1, ν_N = 1.0322 MHz, $eQ = 0.0193\times10^{-24}$ cm^2; where ν_i are Larmor frequencies at magnetic field of the EPR lines B = 335.4 mT (see Fig. 3) and eQ is the electric quadrupole moment. It is clearly seen that the peak at about 14 MHz is pro-

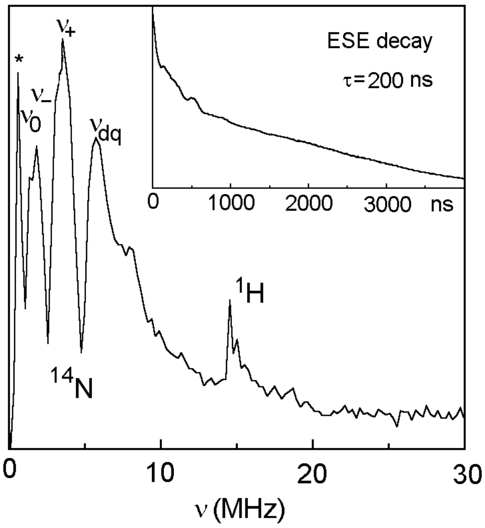


Figure 4. Stimulated three-pulse modulation spectrum (ESEEM spectrum) recorded at 295 K for the excitation of the whole EPR line ($g = 2.0025$, $B = 335.4$ mT) using 48 ns pulses with interval τ = 200 ns. Peaks arise at ^{1}H and ^{14}N magnetic nuclear frequencies. The inset shows weakly modulated ESE amplitude decay.

duced by ^{1}H nuclei. The peak is badly resolved because of large number of protons involved.

The low frequency peaks in Fig. 4 form the pattern characteristic for ^{14}N well recognized for many amorphous systems, especially biopolymers [13,14]. These peaks are characteristic for $\nu_{\rm eff} < K$ at "cancellation condition" $a_{iso} \approx 2\ _{\rm N}$ [15], where $\nu_{\rm eff} = \nu_N + a_{iso}/2$ (a_{iso} is the isotropic hyperfine coupling constant) and $K = e^2Qq/4h$ (eq is the electric field gradient in covalent bond of N-atom). The peaks can be assigned as $\nu_0 = 1.7$ MHz, $\nu_- = 1.8$ MHz, $\nu_+ = 3.5$ MHz and broad asymmetric peak of the double quantum transition at $\nu_{dq} = 5.4$ MHz. The narrow peak at 0.6 MHz, marked by asterisk in Fig. 4, is an artifact of the Fourier transform of non perfectly handled dead-time disturbed ESE decay, due to the lack of the first modulations in ESE decay. The quadrupole parameters can be evaluated from ν_0, ν_- and ν_+ as: quadrupole coupling constant $e^2Qq/h = 3.76$ MHz and asymmetry parameter $\eta = 0.90$. The double quantum line frequency ν_{dq} allows to evaluate the isotropic hyperfine parameter as $a_{iso} = 1.25$ MHz. Both the quadrupole coupling parameters and a_{iso} are among typical values, and the ESEEM pattern indicates that the single ^{14}N contributes. However, a more distant ^{14}N nucleus effect can be also recognized as weakly resolved peaks on the high field slope of the $_{dq}$ line [16,17].

Molecular structure of the chain-end: The cw-EPR and ESEEM data allow to draw conclusions about the geometry of the radical environment. The radical is formed in the last stage of the reaction, when an electron is transferred from NaS$^-$ to pyrrolidone C=O group (Scheme 3). The final oligomer chain-end appears, however, mostly in non-radical neutral form and only about 1% of the chain-ends contain a stable free radical giving strong EPR signals. IR and NMR data describe the neutral form, whereas EPR gives information about the radical form. Unpaired electron of the free radical is localized on a carbon atom, as shown by EPR line parameters. This atom is not bonded to a nitrogen atom, since the resolved hyperfine triplet should be then observed instead of a single narrow EPR line. Thus, the radical is localized on the carbon atom of the carbonyl group, the C–N bond in the ring is broken, and the NMP molecule is bonded to the oligomer chain by CH-group, as shown at right side of (**2**) in Scheme 4. This is confirmed by ESEEM spectrum, which shows that single ^{14}N nucleus is located nearly the radical site. This nitrogen belongs to the NH-group bonded to the phenyl ring. The pyrrolidone nitrogen gives a small effect in ESEEM spectrum only, what confirms that the pyrrolidone ring is broken and nearly linear end-side is formed as shown in Fig. 5.

Neutral form of the oligomer end-side seems to be the result of fast recombination processes at final stage of the reaction. We have found that the radicals disappear rapidly (recombine) in N-methyl-2-pyrrolidone or dimethyl sulfoxide solutions and the frozen solutions do not display EPR signal at all. Thus, we can assume that the neutral oligomer contains a non-broken pyrrolidone ring and the linkage of NMP to the amine group of a 4-hydrazo-diphenylenedisulfide chain appears *via* CH_2-group. This is consistent with IR data, which show a strong band from C=O group, and with the ratio of aromatic to aliphatic protons and the ratio of aromatic to NH protons in NMR spectra.

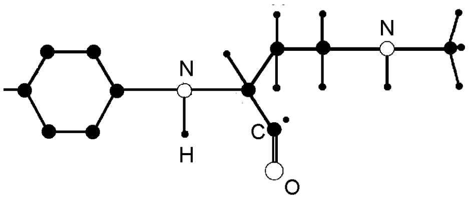


Figure 5. Radical end of the polymer chain formed by N-methyl-2-pyrrolidone molecule with broken C–N bond of the pyrrolidone ring and unpaired electron localized on the carbon of the C=O group.

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