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Formation and reorientation dynamics of nitroxides in the controlled radical polymerisation of styrene initiated by a bisalkoxyamine

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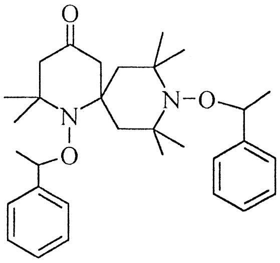
Abstract

The thermal dissociation of the bisalkoxyamine



(denoted StNNSt) releases the styryl St˙ and one of the two isomers of the StNN˙ nitroxide radicals; the former initiates a living chain P˙ and the latter controls the polymerisation by limiting the chain growth. A sequence of dissociation, propagation and recombination reactions produces the StNNP and PNNP bisalkoxyamines as well as a PNN˙ nitroxide. A decomposition side reaction of PNNP leads to HNNP with a hydroxylamine functionality, which by dissociation produces the HNN˙ nitroxide. All these reactions have previously been shown to play a key role in the controlled radical polymerisation of styrene mediated by a dinitroxide biradical [1,2].

The evolution of nitroxide radicals in the course of the bulk polymerisation of styrene at 130 °C initiated by StNNSt, has been followed by ESR at this temperature as well as on several samples cooled down from 130 to 21 °C at different time intervals. The hyperfine coupling parameters and the reorientation correlation times have been obtained from the automated fitting of spectra. As the polymerisation proceeds, the StNN˙ radical initially observed is progressively replaced by PNN˙, characterised by a much longer correlation time, which increases as the chain segmental motion slows down. At high polymer yields (60–80%) the spectra show two components S and F relevant to the slow and fast motional regimes. The S component corresponds to the fraction of PNN˙ embedded in the polymer chain network whereas the F component is assigned to the fraction of PNN˙ moving in free volumes as well as to HNN˙ whose concentration increases till the end of the reaction.

Keywords: Electron spin resonance; Segmental motions; Correlation times

1. Introduction

Recently, we reported the unique behaviour of nitroxide biradicals in the controlled polymerisation of styrene [1,2]. Those dinitroxides have both radical sites of similar reactivity, with a structure close to that of TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl). They were used as mediators in the controlled radical polymerisation of styrene at 130 °C and the rate constants of the various reactions involved in the polymerisation mechanism were determined. It was shown that the typical features of a controlled radical polymerisation were observed in the early stage of the polymerisation, leading to the formation of two-arm

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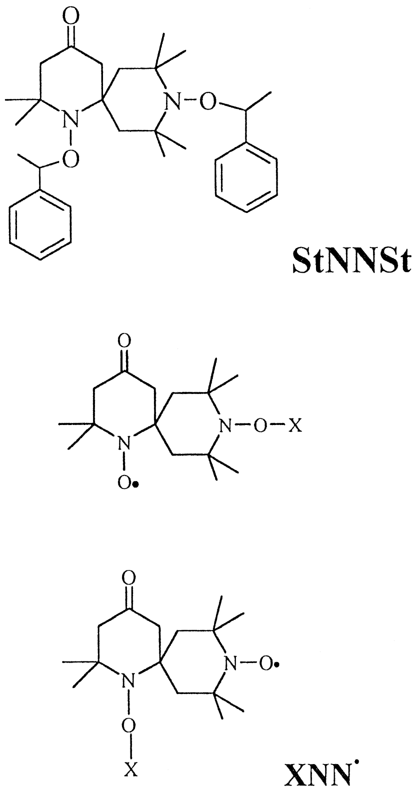


Scheme 1. Formulae of the StNNSt initiator and of the two isomeric $XNN^{\bullet}$ nitroxide radicals. St and NN denotes the styryl and 'TEMPO/TEMPONE' residues, respectively; X = H, St or P (polymer chain). The same notation holds for the ${}^{\bullet}NN^{\bullet}$ biradical (1,9-dioxy-2,2,8,8,10,10-hexamethyl-1,9-diaza-spiro[5.5]undecane-4-one), the StNNP and PNNP bisalkoxyamines and the HNNP polymeric hydroxylamines.

macromolecules, PNNP (see caption to Scheme 1), containing the dinitroxide fragment in its core. At higher conversion, however, continuous decomposition reaction resulted in a break of the two-arm macromolecules into a dead chain having an unsaturated end-group ($P^{=}$) and a chain capped by a modified dinitroxide ($PNN^{\bullet}$). The latter alkoxyamine nitroxide had the free radical site inactivated by conversion into alkoxyamine hydroxylamine (HNNP) (Scheme 2). It has been shown [1,2] that two activation–deactivation equilibria are mainly controlling the polymerisation. The first one (I) involves a propagating macroradical $P^{\bullet}$ and a nitroxide attached to a polymer chain, $PNN^{\bullet}$ (Scheme 1, X = P). For the second one (II) the nitroxide counter-radical is a small one, $HNN^{\bullet}$ (Scheme 1, X = H) resulting from the termination and bearing an hydroxylamine functionality as a reaction product of one of the nitroxide sites.

$$\mathrm{PNNP} \rightleftharpoons \mathrm{PNN}^{\bullet} + \mathrm{P}^{\bullet} \tag{I}$$

$$\mathrm{HNNP} \rightleftharpoons \mathrm{HNN}^{\bullet} + \mathrm{P}^{\bullet} \tag{II}$$

Electron spin resonance (ESR) data were consistent with the existence of at least two different mononitroxides differing by their reorientation correlation time. One was detected in the purified polymer indicating it was attached to a polystyrene chain ($PNN^{\bullet}$) and the other one was recovered in the methanol filtrate (the polymer was precipitated in methanol for purification), indicating that we are dealing with small radicals, presumably $HNN^{\bullet}$ and $StNN^{\bullet}$.

In order to identify these species and to follow their evolution with the reaction time we have performed a detailed ESR study of the styrene polymerisation initiated by the StNNSt model bisalkoxyamine (Scheme 1) at 130 °C which involves the same reaction intermediates as in the polymerisation controlled by the ${}^{\bullet}NN^{\bullet}$ biradical [1,2]. We have determined the concentration and reorientation dynamics of the various nitroxide radicals generated by these reactions, which depend on their size, flexibility and on the polymer concentration. The main purpose of this ESR study was to confirm the reactions of formation and decay of these radicals assumed from the kinetics of the polymerisation of styrene initiated by StNNSt [1,2] (Scheme 2). They are taken from a more extensive reaction scheme given in Refs. [1,2]. The ESR study of this system which generates spin-labelled polymer chains ($PNN^{\bullet}$) provide more additional information on the kinetics than for a polymerisation initiated by a monoalkoxyamine like StNSt where only the $StN^{\bullet}$ nitroxide radical could be observed [3,4].

2. Materials and methods

Freshly distilled styrene 0.01 and 0.02 mol l^{-1} solutions of the bisalkoxyamine StNNSt were introduced into an ESR tube. This tube was thoroughly degassed by three freeze-pump-thaw cycles and sealed off under vacuum.

Two series of ESR experiments have been performed.

(a) Continuous recording of ESR spectra during 5 h at 130 °C. The sample tubes were placed in the variable temperature device of a X band ESR 100 Bruker spectrometer operating at 9.24 GHz, with a microwave power of 2.5 mW and a 100 kHz modulation of amplitude 0.05 mT. The spectra were digitised by means of an acquisition system from Stelar s.n.c., Mede, Italy. It was verified at the end of the experiment that the intensity of the spectra, corrected for its $1/T$ dependence (Curie's law) was unchanged on cooling down the sample from 130 to 21 °C, this temperature being reached in ca. 20 min.

(b) The ESR tube was heated at 130 °C in a thermostated oil bath. At several time intervals, the tube was removed from the bath and the concentration of the nitroxide radicals was monitored by ESR at 21 °C after 30 min. cooling, on a Bruker ESR300 spectrometer operating at 9.45 GHz with a microwave power of 10 mW and a 100 kHz modulation of amplitude 0.1 mT, the spectra being digitized by means of the WINEPR system from Bruker.

$$\mathrm{StNNSt} \rightleftharpoons \mathrm{StNN}\bullet + \mathrm{St}\bullet \tag{1}$$

$$\mathrm{St}\bullet + n\,\mathrm{St} \longrightarrow \mathrm{P}\bullet \tag{2}$$

$$\mathrm{P}\bullet + \mathrm{StNN}\bullet \rightleftharpoons \mathrm{PNNSt} \rightleftharpoons \mathrm{PNN}\bullet + \mathrm{St}\bullet \tag{3}$$

$$\mathrm{PNNP} \rightleftharpoons \mathrm{PNN}\bullet + \mathrm{P}\bullet \tag{4}$$

$$\mathrm{PNNP} \longrightarrow \mathrm{HNNP} + \mathrm{P}^{=} \tag{5}$$

$$\mathrm{HNNP} \rightleftharpoons \mathrm{HNN}\bullet + \mathrm{P}\bullet \tag{6}$$

Scheme 2. Reactions leading to the formation and decay of nitroxide monoradicals. $\mathrm{St}^{\cdot}$ and $\mathrm{P}^{\cdot}$ are the styryl and the chain-propagating radicals, respectively. $\mathrm{P}^{=}$ is a dead polymer chain terminated by a double bond.

In both experiments, the absolute radical concentration was measured at 21 °C by double integration of the spectra and comparison with reference spectra of TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) and TEMPONE (2,2,6,6-tetramethylpiperidone-*N*-oxyl) 10^{-4} M in styrene, recorded with the same modulation and microwave power as for the alkoxyamine/styrene system.

The ESR experiment (b) was performed under the same conditions as the polymerisation kinetic study [1,2]. In that study, the polymerisation was performed by heating the reaction tube at 130 °C in an oil bath. After cooling at room temperature, the content of each reaction tube was poured under stirring into an excess of methanol. The polymer was isolated by filtration, washed with methanol and dried to determine the yield (Y_p) and molecular weight ($\bar{M}_n$). The methanol filtrate and the polymer were analysed by ESR. In all cases, a spectrum characteristic of a mononitroxide was observed in the methanol filtrate but, owing to dilution, its concentration was always too small to be determined. The measurement of the concentration of $\mathrm{PNN}^{\cdot}$ nitroxide radicals in the recovered polymer was quite unreliable, possibly owing to the oxidation of hydroxylamine residues (HNNP). The ESR spectra of dilute polymer solutions in tetrahydrofuran were recorded to determine the dependence of the reorientation correlation time of $\mathrm{PNN}^{\cdot}$ on the conversion yield and molecular weight. Only the radical concentrations determined on sealed ESR tubes have been taken into account in this work. More details on the experimental procedures are given in Refs. [1,2]. Lastly, ESR experiments have been performed on the solid polymer containing $\mathrm{PNN}^{\cdot}$ and on solutions at several concentrations of this polymer in styrene, for molecular weights $\bar{M}_n =$ 17 300, 23 900 and 31 200 Da.

3. Analysis of ESR spectra

At 130 °C as well as at 21 °C, a broad line of ca. 3 mT width at half-height, not removed by baseline correction and underlying the three lines of the nitroxide radical is observed on the integrated experimental spectrum during the first few minutes of reaction (Fig. 1). This signal is assigned to the $^{\cdot}\mathrm{NN}^{\cdot}$ biradical resulting from the cleavage of the two alkoxy bonds of StNNSt; it is not detectable on the recorded first derivative spectra and disappears rapidly.

From the beginning of the experiment, the three narrow lines of nitroxide radicals separated by 1.55 mT are observed. Even after removal of the broad line, the $M_I = \pm 1$ lines are not perfectly symmetric with respect to their intercept with the baseline (Figs. 1 and 2(a)). Spectral simulations by means of methods described below reveal that the nitroxide three lines are the superposition of two

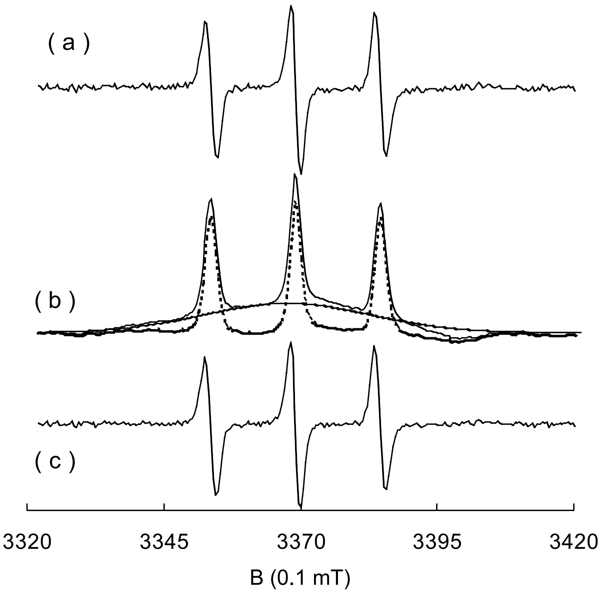


Fig. 1. (a) Spectrum recorded at 21 °C and time $t = 0$; (b) integral of (a) (—), broad line assigned to ˙NN˙ (**—**), difference assigned to StNN˙ between the integral of (a) and the broad line (- - -); (c) derivative of the difference. It is seen that (a) and (c) look practically the same although the concentrations of StNN˙ and ˙NN˙ are almost equivalent.

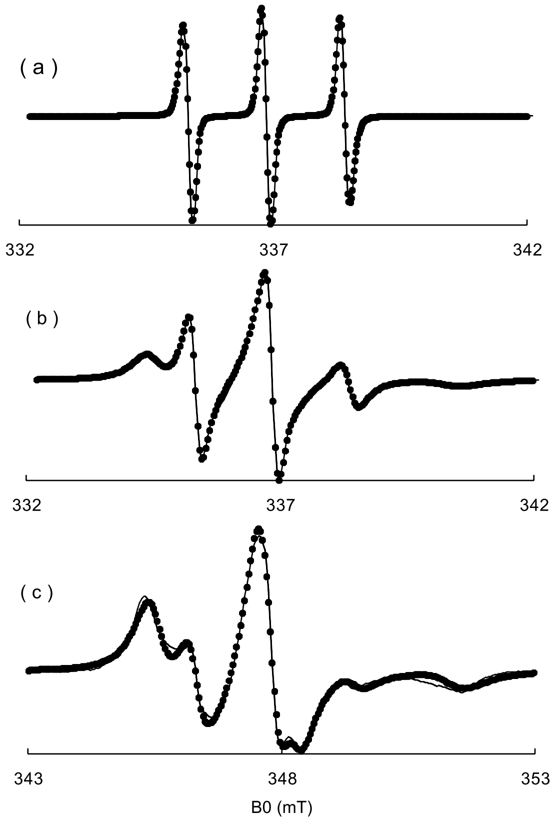


Fig. 2. Experimental (—) and computed (···) spectra at 21 °C ($[\mathrm{StNNSt}]_0 = 0.02\ \mathrm{mol\ l}^{-1}$): (a) After $t = 5$ min reaction, $Y_\mathrm{p} = 0.04$, $\tau_\mathrm{f} = 0.068$ ns, $X_\mathrm{f} = 1$. (b) $t = 850$ min, $Y_\mathrm{p} = 0.79$, $\tau_\mathrm{f} = 0.51$ ns, $\tau_\mathrm{s} = 22.2$ ns, $X_\mathrm{f} = 0.18$, $\nu_\mathrm{ex} = 5.8 \times 10^6\ \mathrm{s}^{-1}$. (c) Spectrum of PNN˙ in polystyrene ($\bar{M}_\mathrm{n} = 23\,900$ Da) solution in styrene, $Y_\mathrm{p} = 0.79$, $\tau_\mathrm{f} = 0.83$ ns, $\tau_\mathrm{s} = 24.2$ ns, $X_\mathrm{f} = 0.05$, $\nu_\mathrm{ex} = 2.2 \times 10^6\ \mathrm{s}^{-1}$.

components of nearly same intensity, same g factor (the $M_\mathrm{I} = 0$ line is symmetric) and of hyperfine splittings 1.521 ± 0.004 and 1.588 ± 0.008 mT, respectively. As they correspond to the same correlation time and to nearly equivalent concentrations, they are assigned to the two isomeric StNN˙ radicals (Scheme 1). At the beginning of the polymerisation process, the low field and central lines are of comparable amplitude whereas the high field line shows a smaller one (Fig. 2(a)), this difference being less perceptible at 130 °C than at 21 °C. Such a spectral shape is significant of nitroxide radicals undergoing a fast quasi-isotropic tumbling (i.e. no privileged axis of reorientation). For ESR measurements at 130 °C, only a slight broadening of the lines is observed as the polymerisation proceeds. On the other hand, when the measurements are done after cooling the samples to 21 °C, one spectral component remains virtually unchanged while the other one broadens rapidly with the reaction time and becomes more and more asymmetric, reaching a limiting shape where two absorption-like lines separated by 5 up to 6.3 mT, characteristic of the slow tumbling regime, appear on each side of the spectrum (Fig. 2(b)).

A quantitative interpretation of the spectra in terms of reorientation correlation times and component fractions was performed, considering three stages:

(i) Two components of same reorientation correlation time τ_f; fast tumbling regime. For a nitroxide radical in X band, the fast tumbling regime is defined by

$$\tau_\mathrm{f} < \left(\gamma_\mathrm{e}\left(a_{zz} - \tfrac{1}{2}(a_{xx} + a_{yy})\right)\right)^{-1} \approx 2\ \mathrm{ns}$$

where a_{xx}, a_{yy} and a_{zz} are the principal components of the nitrogen hyperfine coupling tensor **a**, expressed in magnetic field units and γ_e, the electron magnetogyric ratio.

(ii) Two components with different reorientation correlation times; fast tumbling regime with $\tau_\mathrm{f} < \tau_\mathrm{s} < 2$ ns.

(iii) Two components with $\tau_\mathrm{f} < 1$ ns (fast tumbling) and $\tau_\mathrm{s} > 2$ ns (slow tumbling).

Here and in the following, F and S refer to the motionally unrestricted and restricted sites (e.g. free solvent and polymer coils or chain network) and to the nitroxide species in these sites as well as to the relevant spectral components.

As explained in Section 4, these three stages were observed on spectra recorded at 21 °C but not at 130 °C where only stage (i) could be considered. In stage (iii), the spectral resolution becomes insufficient to distinguish the hyperfine coupling constant a_N of the two components, however, the contribution of the anisotropic coupling to the S component becomes more and more apparent as τ_s increases.

The parameters of interest, namely τ_f, τ_s, the molecular fraction X_f of the F component in cases (ii), (iii) and eventually the exchange rate ν_ex between the F and S sites have been extracted from the automated fitting of the spectra using the Levenberg–Marquardt's optimisation algorithm [5] as reported in Ref. [6].

In the fast tumbling regime, the Lorentzian half-height half-widths dependent on τ_f and on the nuclear magnetic quantum number M_I are

$$\Delta H(M_I) = \frac{1}{\gamma_e T_2(M_I)} = A + BM_I + CM_I^2 \tag{1}$$

where A, B and C are functions of τ (τ_f or τ_s if < 2 ns), of the anisotropies of the **a** and **g** tensors and on the spectrometer frequency [7]. The other contributions to the line-widths, independent of M_I, are the Lorentzian broadening ΔH_L, resulting from the electron spin–spin dipolar and exchange interactions and from the spin-rotation relaxation, as well as the Gaussian inhomogeneous broadening ΔH_G, due to the unresolved hyperfine couplings with a smaller contribution of the field modulation [8]. ΔH_L and ΔH_G are found in the 0.007–0.01 and 0.05–0.07 mT ranges, respectively. It was found that changing the modulation amplitude from 0.05 to 0.1 mT increases ΔH_G by 0.01 mT as measured on the TEMPO and TEMPONE reference samples. It must be pointed out that for very short correlation times, the line-width given by Eq. (1) are much smaller than the sum of ΔH_L and ΔH_G so that the determination of τ is quite inaccurate. Thus, for $\tau = 0.01$ ns one finds $\Delta H(M_I) = 0.0065, 0.0072, 0.0092$ mT.

Besides τ, the adjustable parameters are ΔH_L and ΔH_G, assumed to have the same values for the two spectral components in stages (i) and (ii), and a corrective factor λ multiplying the components of the **a** tensor, which depend on the solution polarity [9]. The radicals formed from the bisalkoxyamine are either of the TEMPO or of the TEMPONE type. The principal values of magnetic tensors adopted in these calculations have been determined from an automated fitting of the spectrum of the TEMPO radical in glassy methylcyclohexane at 100 K, which yields g_{xx}, g_{yy}, $g_{zz} = 2.0096$, 2.0069, 2.0020, $g_0 = 2.0062$ and a_{xx}, a_{yy}, $a_{zz} = 0.634$, 0.644, 3.37 mT, $a_N = 1.55$ mT. Some fittings have been performed using the magnetic parameters of the TEMPONE in glassy toluene [10]: g_{xx}, g_{yy}, $g_{zz} = 2.0096$, 2.0063, 2.0022, $g_0 = 2.0060$, a_{xx}, a_{yy}, $a_{zz} = 0.41$, 0.61, 3.34 mT, $a_N = 1.45$ mT. As the dielectric constant of styrene at room temperature is likely different from those of methylcyclohexane and toluene glasses at low temperatures, the principal values of the hyperfine coupling tensor are rescaled by the factor λ in the automated fitting of the spectra. Choosing the TEMPO or TEMPONE magnetic tensors as initial parameters make no significant differences in the determination of reorientation correlation times. The principal values of magnetic tensors obtained from the fitting of the spectrum of the $\mathrm{PNN}^{\cdot}$ radical in the solid polymer at 100 K are: g_{xx}, g_{yy}, $g_{zz} = 2.0097$, 2.0070,2.0018, $g_0 = 2.0062$ and a_{xx}, a_{yy}, $a_{zz} = 0.780$, 0.485, 3.513 mT, $a_N = 1.593$ mT.

In stage (i), the spectra have been fitted assuming either a single or two correlation times. The agreement between these two determinations of τ is a good criterion to verify that there is no significant contribution of the S component which becomes apparent in stage (ii).

In stage (iii) the slow tumbling of the S component can be treated as a multisite exchange, each site corresponding to a particular orientation of a radical with respect to the magnetic field $\mathbf{B}_0$. In the case of the Brownian rotational diffusion assumed here, the exchange occurs among adjacent sites and the exchange rates are proportional to the diffusion coefficient $D_s = (6\tau_s)^{-1}$. This is the principle of the method of McCalley et al. [11] adopted here. The unit sphere is divided into N zones of area $2\pi \sin(\theta)\Delta\theta$, centred about $\mathbf{B}_0$, θ being the angle between the z-axis of the **a** and **g** tensors and $\mathbf{B}_0$ and $\Delta\theta$, a constant step. For each value of M_I the multisite exchange is expressed by a system of N modified Bloch's equations (MBE) whose solutions yield the complex electron magnetisation for the sampled orientations. The absorption spectrum is obtained by summing the imaginary parts over θ and M_I. There is no clear-cut transition between the fast and slow motional regimes. In the 2 ns $< \tau <$ 4 ns domain, the spectra can be fitted by the two very different methods appropriate to these regimes. The agreement between the parameters determined thereof is a useful criterion of validity.

As pointed out above, we have considered a possible exchange between the S and F sites expressed in the fast motional regime (stage ii) by a system of two MBE for each value of M_I, the exchange rate being defined as

$$\nu_{ex} = X_f K_{FS} = (1 - X_f) K_{SF} \tag{2}$$

K_{FS} and K_{SF} being the probabilities per unit time of the transfer from F to S and from S to F, respectively, which depend on physical properties of the system (viscosity, heterogeneities in the spatial distribution of sites, etc.). In stage (iii) where the S species undergo a slow tumbling motion, the absorption spectrum is obtained by solving a system of $N + 1$ MBE corresponding to the N orientations defined above and to the F species [12]. More details on the computation procedures applied in this work may be found in Refs. 6 and 12.

4. Results and discussion

The spectra recorded in the course of polymerisation at 130 °C (ESR experiment (a), see Section 2) did not allow the detection of transient radicals like $\mathrm{St}^{\cdot}$ and $\mathrm{P}^{\cdot}$. Only two nitroxide radicals were observed with $a_N = 1.532 \pm 0.006$ mT and $a_N = 1.611 \pm 0.0031$ mT. Attempts to fit the spectra assuming distinct reorientation correlation times for these radicals lead to spurious results probably because they are too short to be accurately determined. A value of $\tau = 0.110 \pm 0.013$ ns has been indeed measured for a dilute solution of $\mathrm{PNN}^{\cdot}$ in polystyrene at 21 °C (see Section 2), completely independent of the degree of polymerisation. The activation energy of polystyrene segmental motions being ≈ 28 kJ mol^{-1} [13], τ is expected to be of the order of 0.005 ns at 130 °C as for a small radical like StNN$^{\circ}$. We have therefore fitted the spectra for a single correlation time τ which varies from an initial value of 0.002 to 0.01 ns after 300 min. at 130 °C. The fractional populations of the two nitroxide radicals determined at this temperature are also not reliable so that the discussion below refer to measurements performed at 21 °C (ESR experiment (b)) where the different nitroxide radicals generated during the polymerisation can be more clearly distinguished by their hyperfine coupling as well as by their reorientation correlation time. The important point is that the concentration of these radicals remains unchanged upon cooling the sample from 130 °C as pointed out in Section 2.

The experimental results shown in Figs. 1–5 correspond to an initial concentration of the bisalkoxyamine initiator [StNNSt] $= 0.02$ mol l^{-1} and to measurements performed at 21 °C under the conditions of the polymerisation kinetic study. The symbols t, Y_p and DP will be used to denote the time of reaction (in minutes), the polymer yield (fraction of polymerised styrene) and the degree of polymerisation $((\bar{M}_n/104))$, respectively. Some values of Y_p and DP given below are interpolated from the data of Fig. 5 and from $\bar{M}_n$ values given in Ref. [1,2].

At the beginning of the reaction ($t < 20$ min, $Y_p < 0.1$), the analysis of the spectrum reveals the presence of two nitroxide radicals of same reorientation correlation time $\tau_f < 0.1$ ns likely corresponding to the two isomers of the StNN$^{\cdot}$ radical (Scheme 1) as pointed out in Section 3. During this period the increase of τ_f is significant of an augmentation of the solution viscosity due to the formation of polymer. Afterwards, two superposed signals are detected (stage (ii), 15–20 min $< t < 200$ min, $0.1 < Y_p < 0.55$): an F component assigned to small radicals denoted RNN$^{\cdot}$ (StNN$^{\cdot}$ and possibly HNN$^{\cdot}$) with τ_f steadily increasing up to

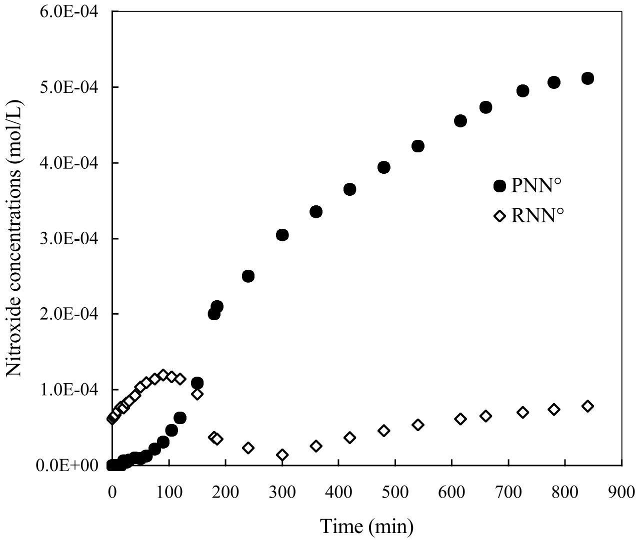


Fig. 3. Concentration of PNN$^{\cdot}$ (polymer) and RNN$^{\cdot}$ (small) nitroxide radical vs the reaction time. [StNNSt]$_0 = 0.02$ mol l^{-1}.

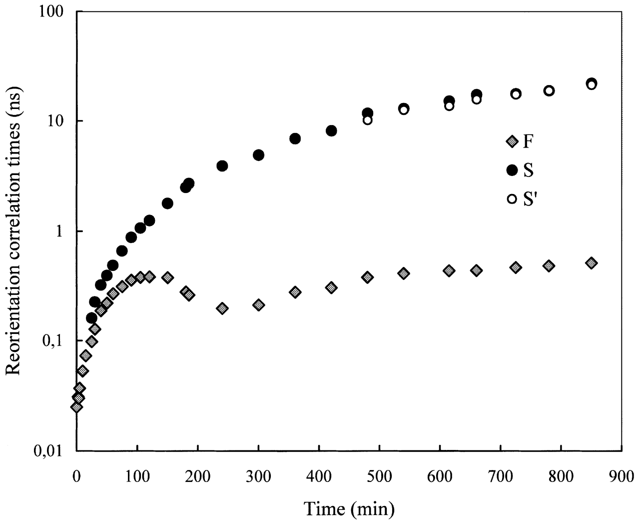


Fig. 4. Reorientation correlation times of the F and S species. The points labelled F and S are obtained from the automated fit of experimental spectra, the points S' are calculated from the total width of the spectra (Eq. (3)). [StNNSt]$_0 = 0.02$ mol l^{-1}.

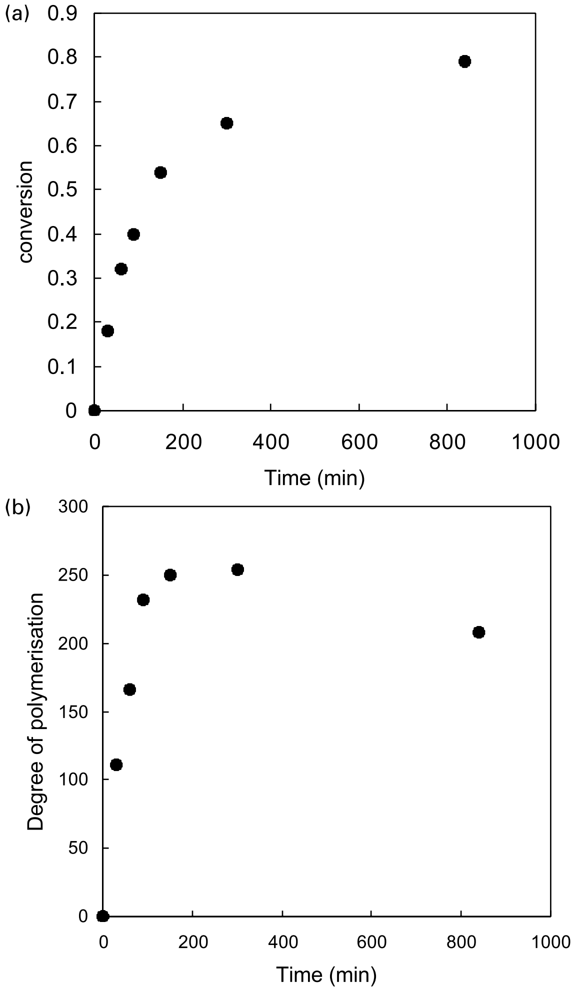


Fig. 5. Conversion and degree of polymerisation for [StNNSt]$_0 = 0.016$ mol l^{-1} taken from Refs. [1,2].

ca. 0.3 ns and a S component showing a steep increase in its fractional population and in its correlation time τ_s (Figs. 3 and 4), still under the fast motional regime. The hyperfine coupling constants of the F and S components are $a_N^F = 1.513 \pm 0.002$ mT and $a_N^S = 1.602 \pm 0.008$ mT. a_N^S is close to the value $a_N = 1.593 \pm 0.014$ measured on the solid polystyrene containing the PNN˙ radical (Section 2). Likewise, the correlation times τ_s are comparable to the correlation times determined on the solutions of recovered polymer for the same values of Y_p (Table 1). The S component is therefore assigned to the polymer chain capped by a nitroxide terminal group (PNN˙).

The difference between a_N^F and a_N^S suggests that the formation of PNN˙ by dissociation of StNNP or PNNP occurs preferentially either on the TEMPO or on the TEMPONE residues of the bisalkoxyamines, possibly on the latter, the most sterically hindered one.

In accord with the so-called persistent radical effect generally occurring in nitroxide controlled polymerisation [3], the overall concentration of nitroxide radicals was found to raise continuously in the course of the reaction. The concentration of the PNN˙ and RNN˙ radicals has been obtained by multiplying the overall concentration of nitroxide radicals taken from Refs. [1,2] by the fractional populations obtained from the fittings of experimental spectra.

A shallow minimum is observed for τ_f and for the concentration of RNN˙ between 200 and 300 min ($Y_p \approx 0.65$) as shown in Figs. 3 and 4. This minimum is assigned to the decay of one of the small radicals, possibly StNN˙ followed by the progressive increase of an other one to be identified. The production of StNN˙ is indeed slowed down by the consumption of the initiator StNNSt whose concentration is reduced to 1% of its initial value after 120 min reaction (dissociation rate constant $k_d = 6.6 \times 10^{-4}\ \mathrm{s}^{-1}$ at 130 °C [1,2]) but this radical is partially regenerated by dissociation of StNNP (Scheme 2, reaction 3).

Table 1
Some values of the fractional populations (X) and reorientation correlation times (ns) in the polymerising system (StNNSt/polystyrene (PS)/styrene) and in reference polymer solutions (PS/styrene) at 21 °C

Polymer molecular fraction	StNNSt/PS/styrene				PS/styrene		
	$[\mathrm{StNNSt}]_0 = 0.02\ \mathrm{mol\ l^{-1}}$				$\bar{M}_n = 17\,300$ Da		
Y_p	τ_s	τ_f	X_f		τ_s		
0.20	0.22	0.13	0.92		0.20		
0.30	0.39	0.22	0.90		0.32		
0.40	0.88	0.33	0.80		0.52		
					$\bar{M}_n = 23\,900$ Da		
	τ_s	τ_f	X_{f1}	X_{f2}	τ_s	τ_f	X_{f1}
0.67	8.1	0.28	0.15	0.08	9.6	0.36	0.16
0.70	13.5	0.38	0.10	0.11	13.2	0.32	0.12
0.79	22.2	0.51	0.05	0.13	24.2	0.81	0.05
	$[\mathrm{StNNSt}]_0 = 0.01\ \mathrm{mol\ l^{-1}}$				$\bar{M}_n = 31\,200$ Da		
Y_p	τ_s	τ_f	X_{f1}	X_{f2}	τ_s	τ_f	X_{f1}
0.78	28.5	0.57	0.10	0.08	28.2	1.2	0.11

In stage (iii) ($300 < t < 850$ min, $0.65 < Y_p < 0.8$) the F and S spectral components are quite clearly distinguishable by their shapes resulting from very different correlation times $\tau_f < 0.5$ ns and $\tau_s > 5$ ns (Fig. 4). The fitting of the spectra is greatly improved by assuming an exchange between the F and S components. The exchange rate ν_{ex} increases from 2×10^6 to $6 \times 10^6\ \mathrm{s}^{-1}$, a slow exchange at the ESR time scale since ν_{ex}/γ_e remains in the 0.01–0.03 mT range.

The correlation times τ_s given by the automated fitting of spectra, varying between 8 and 22 ns from 420 ($Y_p \approx 0.68$) to 850 min ($Y_p \approx 0.80$) reaction are in good agreement (Fig. 4) with the values obtained using the empirical relation

$$\tau_s = a\left(1 - \frac{\Delta}{\Delta_{\mathrm{lim}}}\right)^{-b} \tag{3}$$

proposed by Freed [14] with $a = 5.5 \times 10^{-10}$ s and $b = 1.32$ [12], Δ being the distance between the two outermost lines of the spectra (Fig. 2(b)) and $\Delta_{\mathrm{lim}} = 6.74$ mT its limiting value determined on the TEMPO radical in glassy methylcyclohexane matrix. Such a good agreement is achieved because $\nu_{ex} < 10^7\ \mathrm{s}^{-1}$. A faster exchange between the F and S sites would indeed entail a further significant reduction of Δ. Thus, the S component is hardly affected by the intersite exchange, which results only in a broadening of the F component lines.

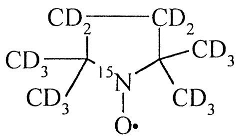
It is worthwhile to compare the values of τ_s to the overall reorientation correlation time τ_R expected for the PNN˙ radical. For a mean chain length $n = \mathrm{DP} = 200$ (Fig. 5), one calculates from Ref. [15] a gyration radius of 7.2 nm and a reorientation correlation time $\tau_R \approx 800$ ns in styrene at room temperature. This is by almost four orders of magnitude larger than the value of $\tau \approx 0.11$ ns measured for a dilute solution of PNN˙ in polystyrene and more generally for correlation times determined in magnetic resonance studies on flexible macromolecules in solutions [16–18]. It is therefore concluded that the values of $\tau \ll \tau_R$ given by ESR are mainly dependent on segmental motions as well as from the rotation of the nitroxide group about its linkage to the macromolecule and explains why after 150 min reaction ($Y_p \approx 0.5$ and $\mathrm{DP} \approx 200$) the reorientation of PNN˙ is still under the fast motional regime. At higher polymer concentrations the microviscosity inside the polymer coils as well as the overlapping of polymer chains [19] contribute to the slowing down of segmental motions, raising τ_s above 2 ns, i.e., in the slow motional regime at $t \approx 180$ min ($Y_p = 0.56$, $\mathrm{DP} = 220$). At the end of reaction ($t = 850$ min, $Y_p = 0.8$), $\tau_s = 22$ ns is some 40 times smaller than the value $\tau_R \approx 800$ ns given above for a dilute polymer solution, although the overall tumbling of macromolecules is probably inhibited at this stage. The restriction of segmental motions could be also assigned to chain entanglements [20–22], but the maximum value $\bar{M}_n = 23\,400$ Da is of the order of magnitude of the critical entanglement molecular weight $M_c = 19\ 100$ Da [23] or 31 000 Da [20] reported for bulk polystyrene, which is expected to be larger in solution [22].

It has been shown by Veskli and Miller [24] that the spin-labelled polystyrene in concentrated solutions shows a composite spectrum with F and S components. In stage (iii), while the S spectral component belongs most probably to the end labelled PNN˙ polymer radical, one cannot say if the F signal corresponds only to the fraction of PNN˙ moving in free volumes [24] or includes a contribution of small nitroxides RNN˙. To remove this ambiguity we have recorded the spectra of PNN˙ in styrene solutions of polystyrene of molecular weight and concentrations comparable with the polymerising system in the highest conversion range ($300 < t < 850$ min, $0.65 < Y_p < 0.8$). The comparison of Fig. 2(b) and (c) shows that for a same polymer concentration X_f is larger in the polymerising system than in the reference polystyrene solution and suggests the presence of RNN˙ (F2 species) in the former one. However, the F2 spectrum cannot practically be distinguished from the one of the PNN˙ reorienting rapidly (F1) so that τ_f represents some intermediate value between τ_{f1} and τ_{f2}. Let us denote X_s the fractional population of PNN˙ undergoing slow motion (S species) X_{f1}, X_{f2} those of the F1 and F2 species and X_s^*, X_{f1}^* the relevant populations in the reference polystyrene solutions. As obviously $X_{f1}/X_s = X_{f1}^*/X_s^*$, the fractional population of RNN˙ is then

$$X_{f2} = 1 - X_s\left(1 + \frac{X_{f1}^*}{X_s^*}\right) \qquad (4)$$

X_s, $X_{f1} + X_{f2}$, X_s^* and X_{f1}^* being given by the fittings of spectra.

When the polymerisation proceeds in the high polymer concentration range, X_{f2} increases up to 0.13 while X_{f1} decreases down to 0.05 (Table 1). This is consistent with the production of HNN˙ resulting from the thermal cleavage of HNNP accumulated in the course of reaction at 130 °C (Scheme 2, reaction 6) and with the reduction of the polymer free volume, restricting the fraction of PNN˙ reorienting rapidly. The exchange rate ν_{ex} between the S and F1 sites measured on concentrated reference polymer solutions is nearly constant and equal to $2 \times 10^6\ \mathrm{s}^{-1}$. For the same polymer concentration range, ν_{ex} increases steadily from 2×10^6 to $6 \times 10^6\ \mathrm{s}^{-1}$ in the polymerising system, in relation with the augmentation of the concentration of small radicals able to diffuse through the fluctuating network of polymer chains. In Table 1, it is seen that at the end of the reaction ($t = 850$ min, $Y_p = 0.79$), $X_{f2} = 2.6X_{f1}$ and that τ_f is significantly smaller in the polymerising system than in the reference polymer solution (0.51 against 0.81 ns). It is therefore estimated that the reorientation correlation time of the small radical is close to 0.5 ns. We have compared this value with the reorientation correlation time τ_{pr} of a small nitroxide probe, the fully deuterated and ^{15}N labelled PROXYL radical.



This probe was introduced in the very viscous solution of polymer cooled down at 21 °C after reaction at 130 °C and the sample was degassed. The spectra were recorded at different times to monitor the diffusion of the probe until showing no further evolution with the time. After removal of the spectra of PNN˙ and RNN˙, τ_{pr} was determined from the fitting of the PROXYL spectrum (Fig. 6), taking g_{xx}, g_{yy}, $g_{zz} = 2.0086$, 2.0062, 2.0026, $g_0 = 2.0058$ and a_{xx}, a_{yy}, $a_{zz} = -0.90$, -0.67, -4.50 mT, $a_N = -2.22$ mT from Ref. [25] after correction for the polarity (see Section 3) and for the $^{15}\mathrm{N}/^{14}\mathrm{N} = -1.4028$ ratio of nuclear g factors. The PROXYL radical being a small semi-rigid entity, τ_{pr} is expected to be proportional to the bulk viscosity, to its molecular volume and therefore to the molecular weight. At

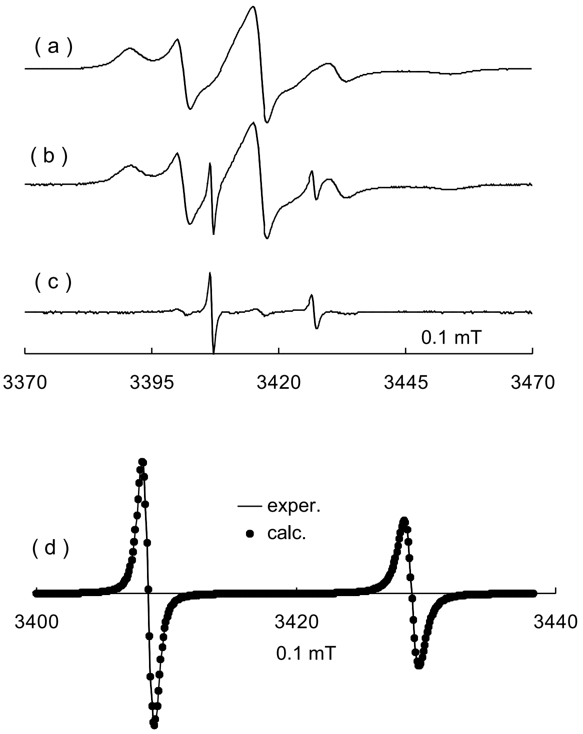


Fig. 6. Determination of the reorientation correlation time of the ^{15}N labelled PROXYL probe. (a) Spectrum of PNN˙ + RNN˙ ($[\mathrm{StNNSt}]_0 = 0.02\ \mathrm{mol\ l}^{-1}$, $t = 850$ min, $Y_p \approx 0.8$) (b) Spectrum of PNN˙ + RNN˙ ($[\mathrm{StNNSt}]_0 = 0.02\ \mathrm{mol\ l}^{-1}$, $t = 850$ min, $Y_p \approx 0.8$) after addition of the ^{15}N labelled PROXYL probe. (c) Difference spectrum between (b) and (a). (d) Fitting of the PROXYL spectrum after complete elimination of the spectrum (a), yielding $\tau_{pr} = 0.28$ ns.

the end of the reaction, when the solution is almost completely filled by the polymer ($Y_p \approx 0.8$), the fitting of the spectrum yields $\tau_{pr} = 0.28$ ns. $\tau_f/\tau_{pr} \approx 1.8$ is then close to the ratio 1.9 expected from the ratio of the molecular weights of the HNN˙ and PROXYL radicals (MW = 295 and 155 g mol^{-1}, respectively). This result supports the assumption that at the end of the reaction, the F2 component mainly corresponds to HNN˙ but the presence of other small radicals as StNN˙ cannot be ruled out.

Similar ESR experiments have been performed at 21 °C on a sample with an initiator concentration $[\mathrm{StNNSt}]_0 = 0.01$ mol l^{-1}. The conversion yield as a function of the reaction time at 130 °C is nearly the same as for $[\mathrm{StNNSt}]_0 = 0.02$ mol l^{-1}, the degree of polymerisation being on the average 1.5 time larger, i.e. DP ≈ 300 for $t = 850$ min and $Y_p \approx 0.8$ [1,2]. The exchange rate between the F and S sites increases from 2×10^6 s^{-1} at the onset of the slow motional regime for the S component to 10^7 s^{-1} at the end of the reaction. No distinction between the F1 (PNN˙) and F2 (RNN˙) rapidly reorienting components have been carried out, except at the end of the reaction where their fractional populations have been estimated (Table 1). The comparison of Fig. 7 with Figs. 3 and 4 shows that the evolutions of component populations and correlation times are not very dependent on the initiator concentration. A feature common to these diagrams is a shallow minimum between 200 and 300 min reaction time ($Y_p \approx 0.5$–0.6) in both X_f and τ_f, suggesting that one of the small radicals contributing to the spectral F component, likely StNN˙, the biggest one, decays while the concentration of HNN˙ formed by reaction 6 (Scheme 2) increases. These minima which nearly coincides with the transition between the fast and slow motional regimes for the S component, possibly correspond to the critical overlap concentration where the fluctuating polymer network extends throughout the solution (see for instance Ref. [19]).

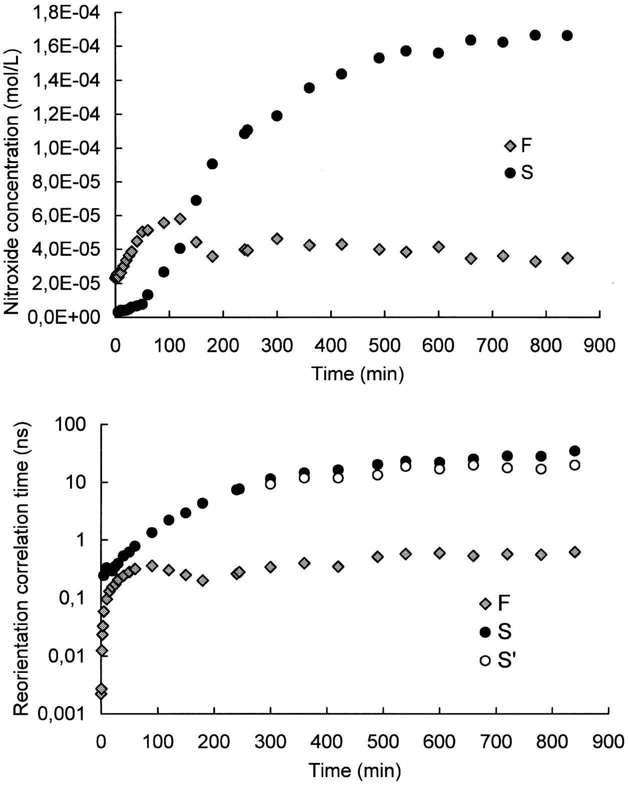


Fig. 7. Concentration and reorientation correlation times of the *F* and *S* species for $[\mathrm{StNNSt}]_0 = 0.01$ mol l^{-1}. The points *F* and *S* are obtained from the automated fit of the spectra, the points *S′* being derived from the total width of the spectrum (Eq. (3)).

5. Summary and conclusion

A study on the polymerisation kinetics of styrene controlled by biradicals or initiated by their bisalkoxyamines derivatives has revealed important changes in the ESR spectra recorded at 21 °C of nitroxide radicals generated in the course of reaction at 130 °C [1,2].

The present work has been performed to identify these radicals and to determine their dynamical behaviour in relation with the kinetics of polymerisation initiated by the thermal dissociation of the StNNSt bisalkoxyamine.

Four steps may be quite clearly distinguished in the evolution of the ESR spectra with the polymer conversion yield:

1. $Y_p < 0.1$: the ESR signal corresponds to the two isomers of StNN˙ resulting from the thermal dissociation of StNNSt, releasing a styryl radical which initiates the polymerisation.
2. $0.1 < Y_p < 0.5$: two nitroxide of significantly different correlation times are observed, StNN˙ and the nitroxide-capped polymer PNN˙, respectively. The latter results from the partially reversible dissociation of bisalkoxyamines StNNP and PNNP formed by the recombination of polystyryl radicals with nitroxides. During this step, StNNSt is completely consumed and StNN˙ decays while the concentration of PNN˙ increases.
3. $0.5 < Y_p < 0.65$: onset of the slow motional regime for a major fraction of PNN˙.
4. $0.65 < Y_p < 0.80$: the ESR spectra show two well defined components S and F relevant to the slow and fast motional regimes, respectively. S corresponds to the PNN˙ fraction embedded in the polymer network and F to the fraction of this radical reorienting in polymer free volumes with an increasing contribution of a small radical, likely HNN˙, formed by thermal dissociation of HNNP.

The steps 1, 2 and 4 correspond to the so-called dilute, semi-dilute and concentrated regimes characterising the polymer solutions [19]. Rapid changes in the ESR spectral shapes suggest that in step 3, a transition in the properties of the solution occurs, possibly related to the overlap of polymer chains. The existence of this transition should be confirmed and its nature determined by more appropriate techniques, e.g. by pulsed field gradient spin-echo experiments [19,26].

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