

In Situ ESR Response to Temperature Evolution of Styrene/Dibenzoyl Peroxide/Di-TEMPO Biradical System

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ABSTRACT: The initial stage of the di-TEMPO (*N,N'*-bis(4-(2,2,6,6-tetramethylpiperidin-1-yloxy))diaminobutane) controlled radical polymerization of styrene was investigated by electron spin resonance (ESR) method in a temperature range of 300–410 K. Processes corresponding to three subsequent temperature subranges 300–360, 360–375, and 375–410 K have been discussed. The decrease of concentration of the di-TEMPO biradicals is faster than for the TEMPO monoradicals in the range 370–390 K. The reduced mobility of capping

groups is postulated to be responsible for the differences between TEMPO monoradical and di-TEMPO biradical mediators. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2036–2041, 2010

Key words: radical polymerization; nitroxide mediated radical polymerization (NMRP); electron spin resonance (ESR); biradicals; polystyrene

INTRODUCTION

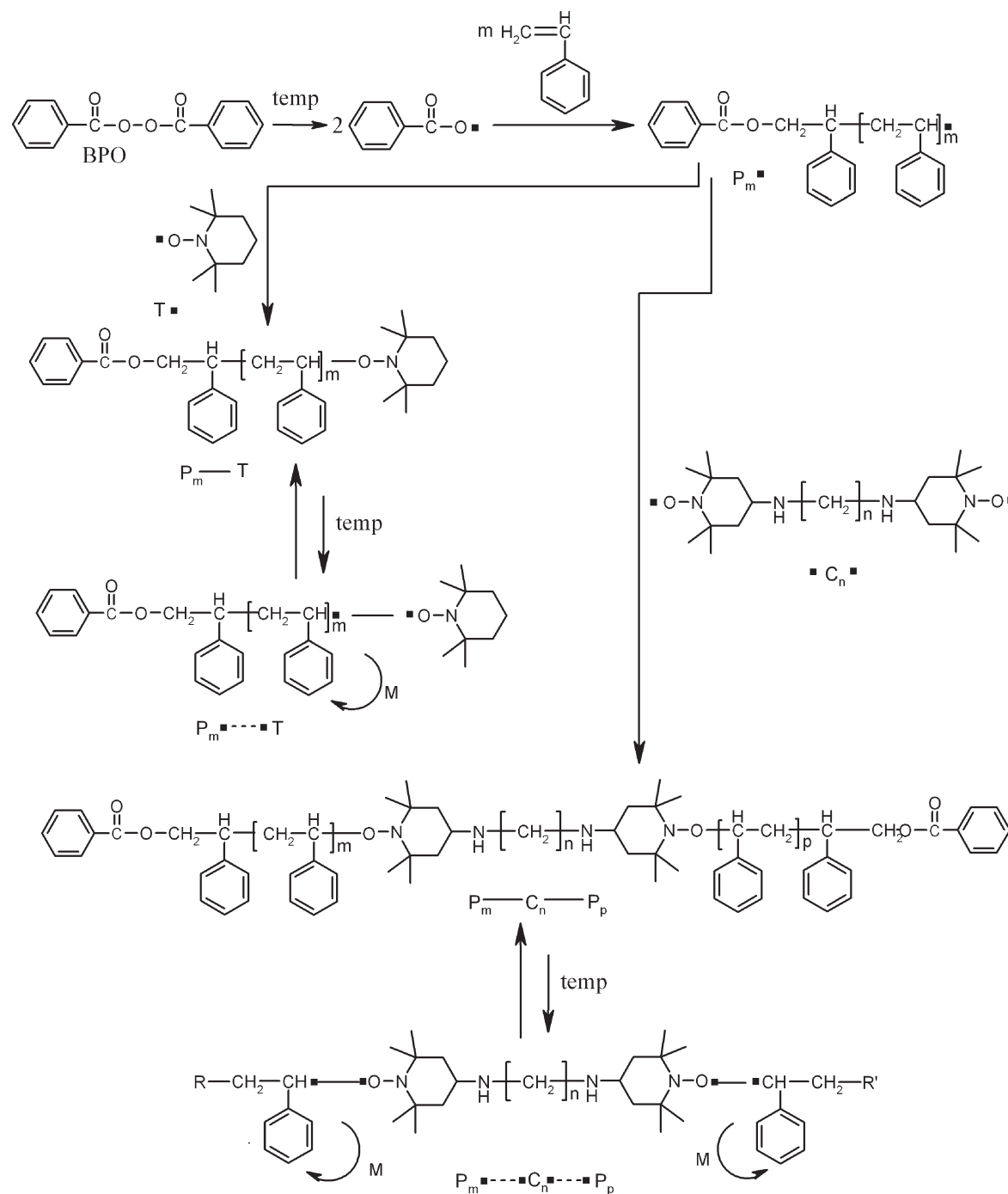
The synthesis of polymers with a tailor-made molecular architecture, molecular weight, and polydispersity index has recently become possible due to controlled/living radical polymerization.^{1–3} In a typical bulk polymerization of styrene,⁴ (2,2,6,6-tetramethyl-1-piperidinyloxy) radical (TEMPO), and dibenzoyl peroxide (BPO) are heated together with monomer at temperature of the range 388–408 K.⁵ (Scheme 1) The reaction is initiated by BPO decomposition into benzoyl radicals, which trigger the polystyrene chain growth ($P_m\cdot$). The control of the nitroxide (T) mediated radical polymerization (NMRP) (left branch reaction in Scheme 1) is governed by the equilibrium between the active polymer radical ($P_m\cdot$) and dormant chain (P_m-T), i.e. by a reversible termination of the growing polymer by TEMPO.^{6–8} At the moment the NO–C bond is broken a new monomer unit is added to the growing polymer chain (P_m). In the case of dinitroxides, (C_n), for example *N,N'*-bis(4-(2,2,6,6-tetramethylpiperidin-1-yloxy)) diaminobutane, (C_4 , di-TEMPO), (Scheme 2), it combines with

two growing polymer chains in two noncorrelated reversible reactions. In this “outside-in” approach the dinitroxide finally resides at the center of the resulting polymer chain $P_m-C_n-P_p$, giving, together with its dissociation products $P_m\cdot$ and $P_m-C_n\cdot$ an unusual bimodal polymer molecular weight distribution.^{9,10} At this point, the ESR method was comparatively rarely used to study kinetics and mechanism of the living polymerization controlled by dinitroxides.^{11,12} It seems to be a quite interesting problem as the dinitroxides show the through-space spin–spin exchange interaction.^{13–15} and therefore it is possible that these interaction affects mediating property of the biradicals. This opinion was strengthened by Braslau and coworkers¹² with suggestion that the near proximity of the second nitroxyl radical enhances the rate of C–ON bond homolysis in dormant chains and allows to perform controlled polymerizations at temperature as low as 70°C. However, it should be raised, that the effect proposed by Braslau and coworkers has been very recently questioned by Marque and Siri.¹⁶ Thus, the role of the dinitroxides in NMRP needs certainly further investigations. In polymerization process the pace of heating the reaction mixture seems to be also important. Usually the polymerization is started by sinking a sample in an oil bath at temperature of the range 388–408 K. However, when the sample is heated slowly from room to polymerization temperature the properties of resulting polymer chains are not the same.¹⁷ Applying the temperature ramp, at the same monomer conversion, the resulting

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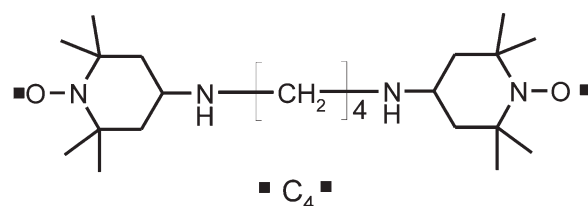
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Scheme 1 Mono- and di-nitroxide controlled radical polymerization of styrene.

polymer chains are shorter. And, to reach the same monomer conversion, longer polymerization time is needed. It seems to be important to learn how the polymerization of styrene develops in the initial stage at rising temperature. This work presents the ESR picture of styrene/dibenzoyl peroxide/(C₄) biradical polymerization system scanned in temperature range of 300–410 K, for concentrations adjusted to ESR sensitivity. To verify the ESR conclusions,



Scheme 2 *N,N'*-bis(4-(2,2,6,6-tetramethylpiperidin-1-yloxy))daminobutane (di-TEMPO, C₄) mediator.

(C₄) biradical controlled polymerization were performed under commonly used conditions. For comparison, some data for polymerization mixture containing TEMPO monoxide radical are also quoted.

EXPERIMENTAL

Materials

N,N'-bis(4-(2,2,6,6-tetramethylpiperidin-1-yloxy))diaminobutane was prepared according to the procedure given previously.¹⁵ TEMPO (98% purity) was used as provided by Aldrich. Dibenzoyl peroxide (BPO, 97% purity) was recrystallized from chloroform/methanol mixture and dried in vacuum in darkness. Styrene was purified according to the common procedures and distilled under reduced pressure before use.

ESR studies

The ESR spectra were recorded using X band Bruker ELEXYS 500 system worked at 9.4 GHz. It was equipped with the nitrogen heating setup. The measurements were performed with 5 K temperature steps of intervals of 6 min. The upper temperature was limited by boiling point of styrene solvent. To the spectrometer the SHQE10115 cavity was mounted. The modulation frequency 100 kHz and modulation amplitude 0.02 mT were applied. This amplitude was small enough for registration of the narrowest signals. The spectra were recorded at 5.12 ms of time constant, at 83.89 s of sweep time and at 7.0 mT of sweep width.

The used microwave power for all measurements was 1 mW. This value ensures the linear work regime far from saturation range. It was verified for TEMPO solution in toluene of similar concentration as for the studied mixtures. The proportionality of spectrum intensity to the active radical concentration was also confirmed for TEMPO radicals. In the samples the di-TEMPO and BPO were strongly diluted (ca.10⁻⁴ M) and their molar concentration ratio was [di-TEMPO]/[BPO] = 0.6. For comparison, samples containing styrene/dibenzoyl peroxide/TEMPO, [TEMPO]/[BPO] = 1.2, were also measured. The ESR spectra were recorded for samples previously degassed in repeated pump-freeze-thaw cycles and sealed in quartz tubes $\phi = 4$ mm under oxygen-free dry argon atmosphere.^{18,19} The recorded ESR spectra were fitted to a sum of two spectra related to interacting and noninteracting spins. Natural isotopes composition of the nitrogen atoms was considered. In fitting, the EasySpin computer program was used. For these two types of the spectra the same isotropic g and A coefficients were valid. Their values are found almost constant with changing temperature

and are equal to $g = 2.0059$ and $A = 1.55\text{--}1.54$ mT (43.5–43.15 MHz). The ESR lines were fitted to pseudo-Voigtian peaks, however, in one registration, their widths were different for interacting and noninteracting spins and were in the range 0.1–0.25 mT. The concentrations of the coupled [*coup*] and uncoupled [*uncoup*] radicals were estimated as proportional to the spectra intensities and presented in arbitrary units (a.u.). The spectra intensity was calculated numerically as the double integral. To normalize the obtained intensities they were corrected by multiplying them by temperature in K. The estimated error of these measurements was temperature dependent and was smaller than 3% for temperature below 370 K. For higher temperature low signal to noise value became substantial.

Polystyrene synthesis

Polymerizations were completed in glass ampoules (capacity ~8 cm³). Mixture of styrene with dissolved BPO ([BPO] = 1 wt % of styrene) and 'C₄' ([di-TEMPO]/[BPO] = 0.6) or TEMPO ([TEMPO]/[BPO] = 1.2) mediator was placed in glass ampoules and degassed by three vacuum-freeze-thaw cycles, sealed under dry argon and immersed in an oil bath preheated to 418 K (135°C). For kinetic analyses, the samples were removed from the reactor after scheduled time and cooled in ice-cold water. The content of the ampoule was dissolved in THF at room temperature. Unconverted styrene and solvent were removed by evaporation under reduced pressure (~10 mbar) at 313 K (40°C) to constant mass. The monomer conversions were determined gravimetrically as a result of at least two independent experiments. The nitroxide radicals contained in the resulting polymer after defined times were detected in ESR studies. For ESR measurements, the polymer samples were dissolved in toluene.

RESULTS AND DISCUSSION

The ESR spectra of the 'C₄' compound dissolved in styrene with BPO registered in temperature range 300–375 K exhibit five visible signals.^{20–22} (Fig. 1). The most intense are three main signals (*a*, *b*, and *c*). Among them, the central peak (*b*) is visibly the strongest. The two weaker and broader signals, *d* and *e*, are situated between the larger ones. The structure of the spectrum for biradical 'C₄' in nonreacting medium (toluene) was discussed in the previous ESR studies.^{13–15} It consists of two sets of signals coming from ESR active radicals i.e. with interacting [*coup*] and noninteracting [*uncoup*] TEMPO units. The stronger lines come mainly from the noninteracting TEMPO moieties and they are expected to be of equal intensity. The in-between

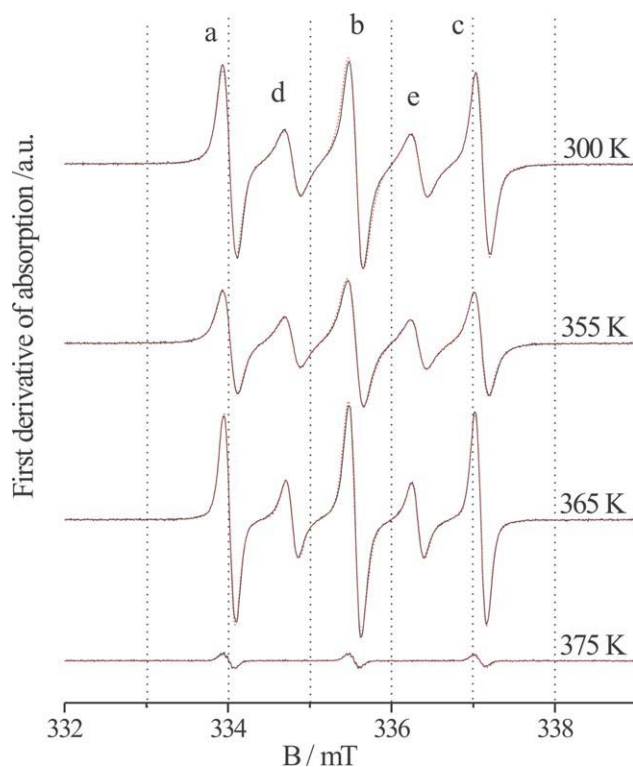


Figure 1 ESR spectra of the di-TEMPO biradical dissolved in styrene with BPO. The dotted lines related to the fitted spectra cover the experimental ones. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

peaks *d* and *e* belong to the coupled radicals and prove the spin–spin interaction of unpaired electrons situated at molecular ends of C_4 . The coupled electrons give five signals that have 1 : 2 : 3 : 2 : 1 intensity ratio. The central and the two external peaks are situated at the same position on the magnetic field scale as the signals coming from separated TEMPO moieties, whereas the two others are placed in-between the former ones. The C_4 biradical has their TEMPO spines coupled when the molecule is in a loop conformation.^{9,13–16} In the solution there is an equilibrium between biradicals being in the loop and in the stretched conformation. In the mixture with styrene and BPO, as described in the present work, there is an additional component, P_m-C_4 monoradical, giving the ESR spectrum with three signals (*a*, *b*, and *c*) identical to that of the uncoupled biradical, C_4 . The estimated concentrations of all radicals active in ESR are shown in temperature scale in Figure 2. The total amount of biradicals contained in the sample, i.e. $[coup] + [uncoup] = [sum]$, slightly decreases at low temperature (300–360 K), its dropping becomes sharper when temperature increases (360–375 K) and at 375 K abruptly extinguishes. The character of this curve reflects the depletion of the nitroxyl units that are neutralized in the polymerization mixture and is correlated with

thermal decomposition of BPO. The homolysis of BPO, increases logarithmically with temperature, i.e. its half-life at temperatures 300, 346, and 364 K were measured to be $>10^4$ h, 10 h, and 1 h, respectively.^{23–25} We assume that the side reaction between BPO and TEMPO (di-TEMPO) radicals can be neglected in comparison to the that of BPO and styrene because of large excess of styrene monomer. The number of auto initiated growing polymer chains at applied temperatures and times is comparatively small so the thermal polymerization of styrene is meaningless either.¹⁰ The concentration of the uncoupled radicals, $[uncoup]$, in the low temperature range (300 – 360 K), stays approximately constant and at temperature > 360 K it shows a slight increase (about 10%). It can be explained by a relative growth of the number of di-TEMPO molecules, P_m-C_4 , which bear the unpaired electron at one end only, whereas the other end is combined with a temporarily dormant polystyrene chain. The concentration of interacting radicals, $[coup]$, falls down when temperature goes up. In the temperature range, 360–375 K, when the number of uncoupled nitroxyls becomes higher, the internally coupled radicals quickly disappear. It is opposite to the previously

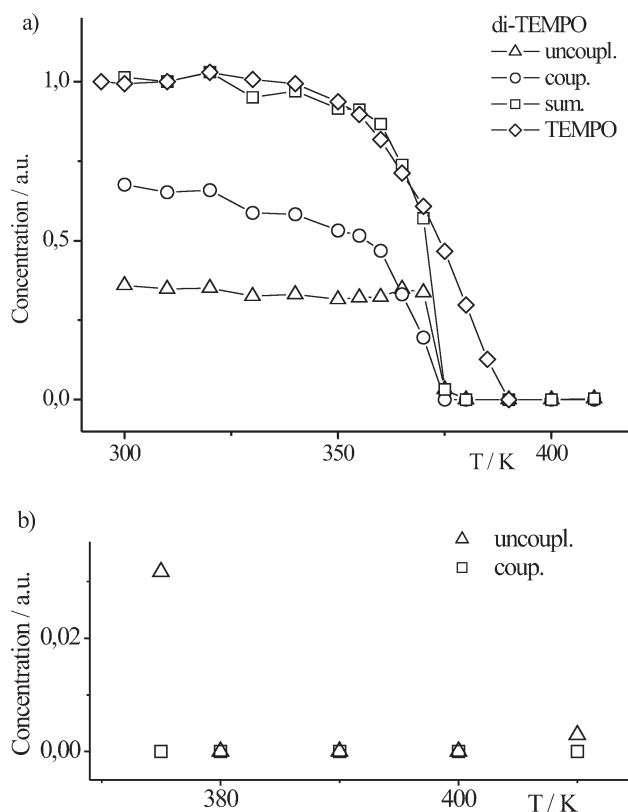


Figure 2 Concentration of the interacting and noninteracting di-TEMPO biradicals in styrene/BPO mixture and, for comparison, the concentration of the TEMPO radical under similar condition (a), magnification of the 370–410 range (b).

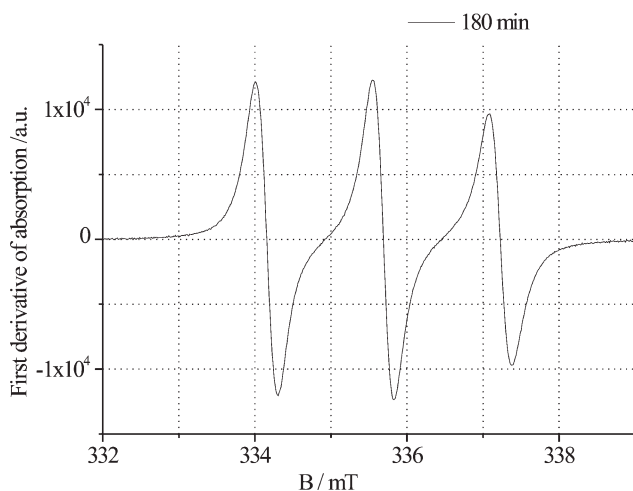


Figure 3 ESR spectrum of toluene solution of polystyrene obtained after 180-min bulk polymerization controlled by di-TEMPO biradicals. The spectrum taken at room temperature.

observed temperature behavior of the biradicals dissolved in the inherent toluene solvent where the number of the biradical loop conformation increases with growing temperature.¹⁵ The falling down of the concentration curve for coupled biradicals in the whole temperature range (300–375 K) reflects that, according to statistical rules, the growing chains, P_p^\cdot , combine more frequently with the biradicals C_4^\cdot than with one side active $P_m-C_4^\cdot$ species. The lack of any increase of the curve shows that the polymer chain $P_m-C_4-P_p$ can rather rarely be split at both side of the $-C_4-$ moiety and cannot liberate the free C_4^\cdot biradical. This supposition was confirmed in final polymer product where the ESR spectrum related to the C_4^\cdot biradicals was not detected. (Fig. 3) Instead, only monoradical $P_m-C_4^\cdot$ spectrum was registered, irrespectively of polymerization time (50–300 min). The negligible concentration of biradicals in the binitroxide controlled polymerization was previously postulated by Huang et al.¹⁰ So, it shows that the macromolecule $P_m-C_n-P_p$ brakes at one end only and therefore the growth of polymer chain takes place rather at one side than at both ends simultaneously. Starting above 375 K the all di-TEMPO radicals disappear (the temperature range 375–410 K).

Comparing the concentration curves for di-TEMPO and TEMPO radicals that are applied in polymerization process (Fig. 2), it can be noticed that with rising temperature to 370 K the decrease of both radicals is similar. At higher temperature (370–390 K), the di-TEMPO radicals extinguish faster. For monoradicals $P_m-C_4^\cdot$, above 375 K, the abrupt quenching is observed, whereas the TEMPO radicals are still present. One of the explanations is a reduced mobility of the capping group, $P_m-C_4^\cdot$, due to its much higher molecular mass, when compared to the smaller and very mobile TEMPO molecule.²⁶

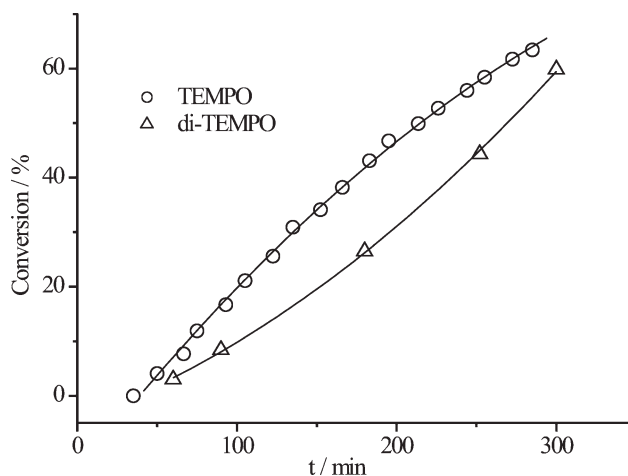


Figure 4 Monomer conversion in radical controlled polymerization of styrene in di-TEMPO/BPO and TEMPO/BPO systems at temperature 408 K; solid lines— guide for eyes.

The heavier $P_m-C_4^\cdot$ radicals diffuse away out of the “cage” more difficult and easily reintegrate with P_p^\cdot to $P_m-C_4-P_p$ again. This phenomenon makes the concentration of the $P_m-C_4^\cdot$ radicals lower and, in consequence, reduces the EPR signals. The bigger number of dormant polymer chains $P_m-C_4-P_p$ results in lower concentration of P_p^\cdot and therefore slower polymerization rate. This explanation is in agreement with the observed weaker monomer conversion for the di-TEMPO biradical system in comparison to that controlled by the TEMPO monoradical. (Fig. 4) The lower monomer conversion suggests that in the polymerization process with the di-TEMPO mediator the mobility of $P_m-C_4^\cdot$ can be governed by viscosity of the reaction mixture. Whereas for the TEMPO

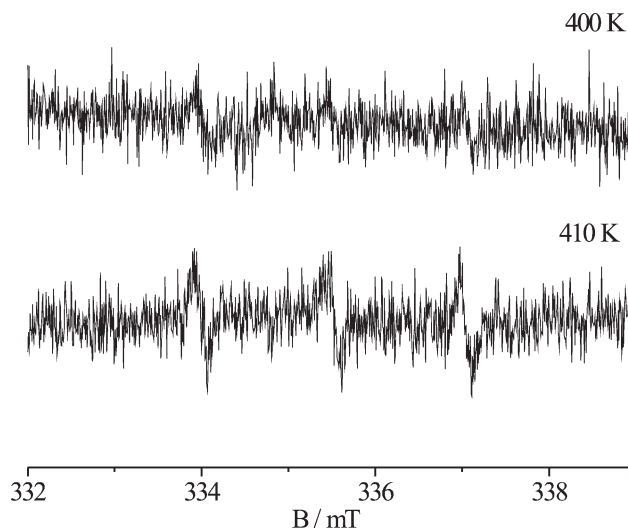


Figure 5 ESR spectrum of di-TEMPO biradicals contained in styrene/BPO system polymerized at temperature 408 K and dissolved in toluene; registration condition are identical as for Figure 1.

radical system, any diffusion controlled effects on polymerization have been excluded.²⁷

When heated to 410 K, the sample gives again three tiny ESR signals of uncoupled di-TEMPO radicals (Fig. 5). They originate from breaking one of the HC—ON bonds in dialkoxyamine $P_m-C_n-P_p$, as shown in Scheme 1. The radical products of thermal decomposition of the polymer chains after heating are usually of very low concentration²⁶ and have been reported to be isolated by GPC methods.^{9,10}

CONCLUSIONS

The presented ESR studies elucidate the processes of the di-TEMPO controlled radical polymerization in the styrene/BPO system, which has been observed at raising temperature in the range of 300–410 K. It shows that the concentration of the biradical mediator, C_4 , falls down being replaced by P_m-C_4 radicals. At heating to temperature of 375 K the growing polymer radicals P_p are deactivated by reaction with capping groups P_m-C_4 that results in dormant $P_m-C_4-P_p$ forms. At further rising temperature above ca. 400 K, statistically, one of the two P—C₄ bonds in macromolecule $P_m-C_4-P_p$ is broken. It allows the polymer chains to grow again at one side of the central dinitroxide moiety. In the styrene polymerization mixture at high temperature as well as in final polymer product the coupled di-TEMPO radicals were not detected, so, the discussed in literature^{9,16} peculiar influence of dinitroxide mediator in the loop conformation on the polymerization reaction was not found. From the EPR studies it appears that there are differences in mediating properties of TEMPO and di-TEMPO radicals. For the biradical controlled system the di-TEMPO mediator is deactivated more quickly than it is for the TEMPO monoradical, especially in the range 370–400 K. It can result from the lower mobility of the di-TEMPO P_m-C_4 radical that is too heavy to drift away fast from the reaction center. In consequence the polymerizing chains are easily capped by the long mediator. It makes the chain growth slower. This kinetic effect was confirmed by time dependent monomer conversion.

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