Synthesis of Oxazoline-Terminated Polystyrene via Controlled-Radical Polymerization

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ABSTRACT: Two novel bis(1,3-oxazoline-2-yl)-functionalized azo initiators were prepared, and their half-lives were determined by UV spectroscopy. These initiators were used in conjunction with 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) to afford controlled-radical styrene polymerization. Polymerization kinetics, molar mass versus conversion dependence and polydispersities with varying [TEMPO]/[initiator] ratios were examined, and the degree of endgroup functionalities was determined by NMR, FT-IR, endgroup titration and size exclusion chromatography (SEC) data. Well-defined narrow-distributed mono-(1,3-oxazolin-2-yl)-terminated polystyrenes with molar mass varying between 1000 and 50 000 with polydispersities of 1.2−1.3 were obtained. The reactivity of the oxazoline moiety was proven by reacting monooxazoline-terminated polystyrene with monocarboxy-terminated polystyrene. Increases in molar mass and the formation of ester amide coupling groups, resulting from the reaction of oxazoline with carboxylic acid endgroups of polystyrene were monitored by means of SEC and FT-IR. Oxazoline endgroup conversion increased with decreasing polystyrene molar mass. Kinetics of the ester amide formation showed Arrhenius-type behavior. The activation energy of melt-phase ester amide formation was determined to be 65 kJ/mol.

Introduction

The synthesis of well-defined polymer architectures and polymers with narrow molar mass distribution represents a key challenge in industrial and academic research.[1] For many years the industrially important free-radical polymerization processes did not meet the requirements of living polymerization because of termination and chain transfer reactions.[2] Recent advances have led to the development of controlled-radical polymerization as a very versatile new synthetic tool to tailor new polymers which are not available by means of conventional living ionic polymerization. Taming the radical polymerization process was achieved by means of rapid equilibrium between dormant and active chain ends involving interactions of the propagating polymer radical and stable radicals such as 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) or paramagnetic transition-metal complexes, respectively.[3] Examples for such polymers synthesized by stable free-radical polymerization are new linear polymers,[4] block copolymers,[5,6] new hyperbranched polymers and dendritic block copolymers,[7] as well as various polymers with new functional endgroups.[6,8] To introduce endgroups, functional initiators are applied in TEMPO-based controlled-radical polymerization processes. Hawker et al. prepared adducts of styrene, TEMPO, and benzoyl peroxide or other functionalized initiators, which he called unimolecular initiators.[8] Recently, it was demonstrated that well-known functional azo initiators can be used successfully in conjunction with TEMPO to produce well-defined polystyrene and poly(styrene)-*block*-poly(styrene-*co*-acrylonitrile) with one functional endgroup (bimolecular initiators).[6] The use of functional azo initiators circumvents the need for preparing special TEMPO adduct-based initiators and is very versatile because a wide range of functional azo initiators are commercially available.

Monofunctional polymers represent telechelics that can stabilize the morphology of copolymers formed during melt blending of immiscible polymers.[9] In particular, oxazoline-functional polymers represent attractive intermediates in reactive processing applications.[10] Oxazolines can react with carboxylic acids within a few minutes at elevated temperatures to afford ester amide groups in very high yield.[11] This clean reaction can be monitored by means of FT-IR spectroscopy.[12] Oxazolines were introduced as endgroups in various liquid rubbers using endgroup conversion reactions.[13] Sivaram and Khisti reported the synthesis of monooxazoline-terminated poly(methyl acrylate) by anionic polymerization using ionic oxazoline initiators.[14] To our knowledge, no other narrowly distributed monooxazoline-terminated polymers have been reported. Moreover, there are no reports on oxazoline-functional azo initiators which are of special interest for applications in controlled-radical as well as free-radical polymerization processes and production of new oxazoline-functionalized polymers as intermediates in reactive processing.

Here we report the synthesis of two novel bis(1,3-oxazolin-2-yl)-functionalized azo initiators with different half-lives. These initiators were then used in controlled-radical polymerization of styrene to obtain new well-defined narrowly distributed monooxazoline-terminated polystyrenes. Polymerization kinetics, molar mass versus conversion dependence, and polydispersities with varying [TEMPO]/[initiator] ratios were examined, and

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the degree of endgroup functionalities was determined by NMR, FT-IR, endgroup titration, and size exclusion chromatography (SEC) data. The reactivity of the oxazoline moiety was proven by reacting mono(1,3-oxazolin-2-yl) terminated with monocarboxy-terminated polystyrenes, which was also synthesized by controlled-radical polymerization. The coupling reaction occurs via ester amide formation between oxazoline and carboxylic acid endgroups. This reaction, which takes place in the homogeneous polystyrene melt, was studied by FT-IR spectroscopy and size exclusion chromatography. Reaction kinetics was measured to study the influence of molar mass and temperature on the conversion of endgroups.

Experimental Section

Materials. Styrene (Fluka) was refluxed and distilled over $LiAlH_4$ at 43 °C and 20 mbar. Acrylonitrile (Fluka) was distilled over CaH_2 at 33 °C and 200 mbar. 2,2′-Azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (Wako Chemicals), tetrahydrofuran (THF), methanol, acetic acid, $HClO_4$ (Riedel-de Haen), 4,4′-azobis(4-cyanopentane carboxylic acid), TEMPO, KOH, $SOCl_2$, and all other chemicals were obtained from Fluka and used without further purification.

Synthesis of Azo Initiators and Their Half Lives. *2-(Hydroxypentyl)-1,3-oxazoline* was synthesized as described elsewhere.[15] *4,4′-Azobis(4-cyanopentane carboxylic acid)-[5-pentyl-2-(1,3-oxazoline)]ester (**OxaI**).* At 0 °C, 4-dimethylamino pyridine (DMAP) (0.140 g, 1.15 mmol) and dicyclohexylcarbodiimide (DCC) (4.544 g, 0.022 mol) were added to a solution of 4,4′-azobis(4-cyanopentane carboxylic acid) (2.806 g, 0.010 mol) and 2-(hydroxypentyl)-1,3-oxazoline (3.459 g, 0.022 mol) in tetrahydrofuran (20 mL) and dichloromethane (50 mL). Stirring was continued for 4 h. After filtration and removal of the solvents by rotary evaporation at temperatures below 30 °C, the crude product was purified by column chromatography (CH_2Cl_2/methanol/triethylamine: 97/3/1). After drying in a vacuum at room temperature for 24 h, 3.79 g (7.2×10^{-3} mol, 72% conversion) of **OxaI** was obtained. ^{1}H NMR ($CDCl_3$): δ = 4.2 [t, CH_2−N (ring), 4H], 4.1 [t, (O═C)−O−CH_2−, 4H], 3.8 [t, CH_2−O(ring), 4H], 2.5 [m, (CH_3)C(CN)−CH_2−CH_2−(C═O), 8H], 2.29 (t, −CH_2−oxazoline, 4H), 1.6 [(CH_3)C(CN) and CH_2−CH_2−CH_2, 18H]. ^{13}C NMR ($CDCl_3$): δ = 171.403 [(O═*C*)−O−CH_2−], 168.27 [N═*C*−O (ring)], 117.49 (*C*N), 71.94 [(CH_3)-*C*(CN)], 67.20 [*C*H_2−N (ring)], 64.99 [(O═C)−O−*C*H_2−], 54.37 [*C*H_2−O (ring)], 34.93 [−*C*H_2−(C═O)], 33.20 [(O═C)−O−*C*H_2−*C*H_2], 30.93 [(CH_3)C(CN)−*C*H_2], 27.78 (−*C*H_2−oxazoline), 25.56, 25.53 [(O═C)−O−CH_2−CH_2−*C*H_2−*C*H_2], 23.99 [(*C*H_3)C(CN].

2,2′-Azobis[2-methyl-N-(2-chloroethyl)propionamide]. Thionyl chloride (50 mL, 0.670 mol) was added dropwise to a cooled (0 °C) suspension of 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)-propionamide] (38.64 g, 0.134 mol) in dichloromethane (180 mL), over 30 min. The reaction mixture was allowed to warm to room temperature and stirring was continued for 18 h. The precipitate was filtered off, washed with water, and dried in a vacuum oven at room temperature for 24 h. Cyclohexane (250 mL) was added to the liquid phase, and the precipitate which formed at 0 °C was filtered off and dried. The residual liquid phase was evaporated at 30 °C, and the resulting precipitate was recrystallized and dried. All three fractions yielded 2,2′-azobis[2-methyl-*N*-(2-chloroethyl)propionamide] (27.6 g, 0.085 mol, 63% conversion). Elemental analysis: $C_{12}H_{22}N_4O_2Cl_2$ (325.24) calcd (found): C, 44.32 (44.50); H, 6.82 (6.93); N, 17.32 (17.55). ^{1}H NMR ($CDCl_3$): δ = 7.3 [s, (O═C)−N*H*−, 2H], 3.7 (m, NH−CH_2−CH_2−Cl, 8H), 1.3 [s, (CH_3)$_2$−C, 12H]. ^{13}C NMR ($CDCl_3$): δ = 174.0 [(O═*C*)−NH], 74.8 [(CH_3)$_2$−*C*−], 44.1 (−CH_2−Cl), 40.9 (NH−CH_2−), 23.0 [(*C*H_3)$_2$−C)].

*2,2′-Azobis[2-(1,3-oxazoline)propane] (**OxaII**).* A solution of KOH (1.74 g, 31.0 mmol) in methanol (20 mL) was added dropwise to a solution of 2,2′-azobis[2-methyl-*N*-(2-chloroethyl)propionamide] (2.00 g, 6.15 mmol) in methanol (10 mL) at room temperature. The reaction mixture was stirred for 6 days, and after removal of methanol by rotary evaporation at 30 °C, column chromatography (cyclohexane/methanol/triethylamine: 92/8/1) yielded **OxaII** (1.01 g, 4.00 mmol, 65% conversion). Elemental analysis: $C_{12}H_{20}N_4O_2$ (252.16) calcd (found): C, 57.12 (57.21); H, 7.99 (8.05); N, 21.20 (21.54). IR: ν [cm^{-1}] = 1654 (C═N), 1250 (C−O), 970, 920, 890. ^{1}H NMR ($CDCl_3$): δ = 4.3 (t, CH_2−N, 4H), 3.9 (t, CH_2−O, 4H), 1.5 [s, (CH_3)$_2$−C, 12H]. ^{13}C NMR ($CDCl_3$): δ = 169.9 (O−*C*═N), 70.3 [(CH_3)$_2$−*C*−], 67.8 (*C*H_2−N), 54.3 (*C*H_2−O), 23.2 [(*C*H_3)$_2$−C].

The half-lives of the azo initiators were measured by UV spectroscopy (Kontron Instruments, Uvikon 933). The initiators were dissolved in triethylene glycol dimethyl ether (1 wt %). Samples were taken after different times of isothermal treatment at 78 °C. The decrease of the extinction E at 365 nm was related to the initial value E_o.

Polymerizations. *Preparation of Monooxazoline-Terminated Polystyrene (**PSOxaII**).* 2,2′-Azobis[2-(1,3-oxazoline)-propane] (0.188 g) and TEMPO (0.116 g) were dissolved in 20 mL of styrene and degassed by two freeze−pump−thaw cycles using argon as the inert gas. The flask was immersed into an oil bath at 140 °C for 12 h, and samples were taken at intervals. The samples were dissolved in THF, precipitated from methanol, and dried in a vacuum at 60 °C for 12 h. *Preparation of Monocarboxy-Terminated Polystyrene (**CTPS**).* 4,4′-Azobis(4-cyanopentane carboxylic acid) (0.813 g) and TEMPO (0.453 g) were dissolved in 80 mL of styrene and degassed by two freeze−pump−thaw cycles using argon as the inert gas. The flask was immersed into an oil bath at 140 °C for 12 h, and samples were taken at intervals. The samples were dissolved in THF, precipitated from methanol, and dried in a vacuum at 60 °C for 12 h.

Reaction of End-Functionalized Polymers. A mixture of 15 mg (2.5 mmol) of **CTPS** and 15 mg (2.5 mmol) of **PSOxaII** was dissolved in THF and transferred to a KBr disk. After removal of the solvent by drying in a vacuum at 60 °C for 3 h, the blend was tempered at 200 °C for 60 min.

Polymer Characterization. Size exclusion chromatography (Knauer Mikrogelset A20) was used to determine molar mass and molar mass distributions, M_w/M_n. The solvent was chloroform at 35 °C, and polystyrene standards were used for calibration. Conversion (mol %) was determined by ^{1}H NMR spectroscopy (300 MHz; $CDCl_3$; Bruker ARX 300). FT-IR spectroscopy was carried out with a Bruker IFS 88. Elemental analysis was performed on an elemental analyzer CHN 2400 (Perkin-Elmer). For titration, a Mettler Titrator was used. The oxazoline-terminated polymers were dissolved in THF/acetic acid, and the resulting acetate was titrated with a 0.01 molar $HClO_4$ solution in methanol.

Results and Discussion

Synthesis of Bisoxazoline Azo Initiators. The aim of this work was the synthesis of well-defined oxazoline-functionalized polymers via a free-radical and controlled-radical polymerization mechanism. It is well-known that controlled-radical polymerization using difunctional azo initiators and TEMPO yields well-defined polymers with one functional endgroup derived from the functional initiator. To synthesize monooxazoline terminated polymers it is necessary to produce bisoxazoline-functionalized azo initiators. There have not been any reports on free-radical polymerization using oxazoline-functionalized initiators. Therefore, two novel bisoxazoline-functionalized azo initiators, as displayed in Figure 1a,b, were synthesized. The length of the spacer between the azo and oxazoline groups was varied. In **OxaI**, the azo and oxazoline groups are separated by a pentylpropionate spacer, whereas in **OxaII**, the oxazoline moiety is adjacent to the carbon atom bearing the azo group.

Figure 1a shows the synthesis of **OxaI**, which is achieved by esterification of 2-(hydroxypentyl)-1,3-oxazoline[15] with 4,4′-azobis(4-cyanopentane carboxylic acid). **OxaII** was synthesized by reacting 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] with $SOCl_2$ at

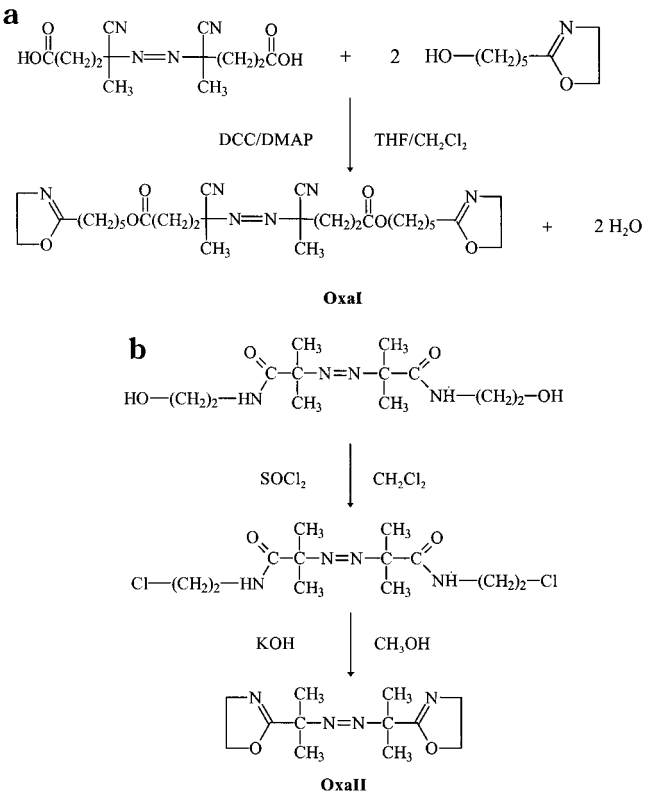

Figure 1. Synthesis of (a) 4,4′-azobis(4-cyanopentane carboxylic acid)-[5-pentyl-2-(1,3-oxazoline)]ester, **OxaI**, and (b) 2,2′-azobis[2-(1,3-oxazoline)propane], **OxaII**.

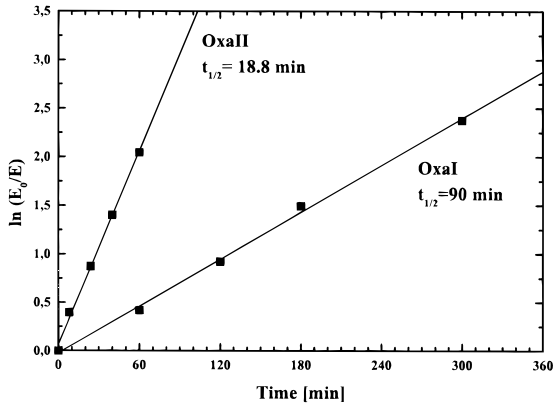

Figure 2. First-order decay of **OxaI** and **OxaII**: correlation of $\ln(E_0/E)$, where E_0 is the UV extinction at 365 nm of the initial initiator solution and E is the extinction after isothermal treatment at 78 °C.

0 °C and treating the resulting 2,2′-azobis[2-methyl-*N*-(2-chloroethyl)propionamide] with KOH to form **OxaII**.

The half-lives $t_{1/2}$ of **OxaI** and **OxaII** were determined by UV spectroscopy. The initiator decay is detected by the decrease of the adsorption of the azo group at 365 nm. Figure 2 depicts the first-order decay of the azo initiators at 78 °C. At this temperature, **OxaI** has a half-life of 90 min, and **OxaII** has a half-life of 18.8 min. For comparison, it should be mentioned that azobisisobutyronitrile (AIBN) has a half-life of 95 min at 78 °C, thus the half-life of **OxaI** is comparable to AIBN but **OxaII** has a much shorter half-life than AIBN. This indicates that the exchange of the nitrile group by oxazoline groups has a destabilizing effect on the C−N bond.

Controlled-Radical Polymerization with Bisoxazoline Azo Initiators. Controlled-radical polymerization of styrene was performed in bulk under argon atmosphere with bisoxazoline azo initiators (**OxaI** and **OxaII**) and TEMPO at 140 °C to produce monooxazoline-terminated polystyrene. Veregin and MacLeod et al. showed for the benzoyl peroxide BPO/TEMPO system that the [TEMPO]/[initiator] molar ratio has an influence on polymerization kinetics, molar mass, and polydispersities.[16] They found that [TEMPO]/[BPO] molar ratios between 1.1 and 1.3 gave best results regarding controlled-radical polymerization behavior. They concluded that there exists a self-correcting mechanism which adjusts the number of growing chains. Regardless of the initial nitroxide/initiator level, the system moves toward an equilibrium concentration of free nitroxide. For the TEMPO/4,4′-azobis(4-cyanopentane carboxylic acid) system, it was shown that a ratio of 1.0 results in a well-controlled radical polymerization.[6] To determine the optimum [TEMPO]/[initiator] molar ratio for the TEMPO/**OxaI** and TEMPO/**OxaII** systems, polymerizations were performed with different [TEMPO]/[initiator] ratios of 0.7, 1.0, 1.2, 1.4, 1.6, and 2.0, respectively. The concentration of TEMPO was held constant, and the initiator concentration was varied. The results are shown in Figure 3a,b. For the TEMPO/**OxaI** system, it can be seen that the ratio of 1.4 yields a linear $\ln([M_0]/[M])$ versus time relationship up to about 480 min, with first-order kinetics between 0 and 8 h when 80% conversion was reached. Deviations at higher conversions may be due to irreversible decomposition of PS-TEMPO adducts after long reaction times. Viscosity may also play an important role. Polymerization of styrene was also carried out with **OxaII**. Here the [TEMPO]/[**OxaII**] molar ratio of 1.6 gave optimum controlled-radical polymerization behavior as evidenced by a linear $\ln([M_0]/[M])$ versus time dependence up to 86% conversion. These different [TEMPO]/[initiator] molar ratios can be explained by different initiator efficiencies. During the initiation period, it is important that the number of moles of formed radicals is equal to the initial molar amount of TEMPO. If the number of

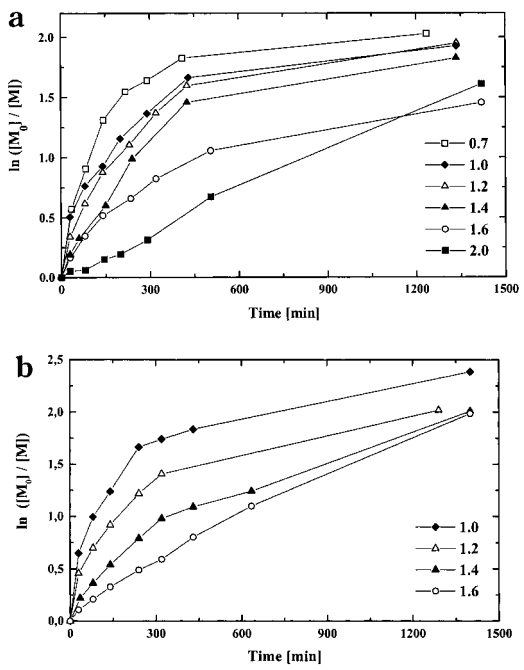

Figure 3. Oxazoline-terminated polystyrene: correlation of $\ln([M_0]/[M])$ with time for different [TEMPO]/[initiator] ratios at 140 °C for (a) **PSOxaI** and (b) **PSOxaII**.

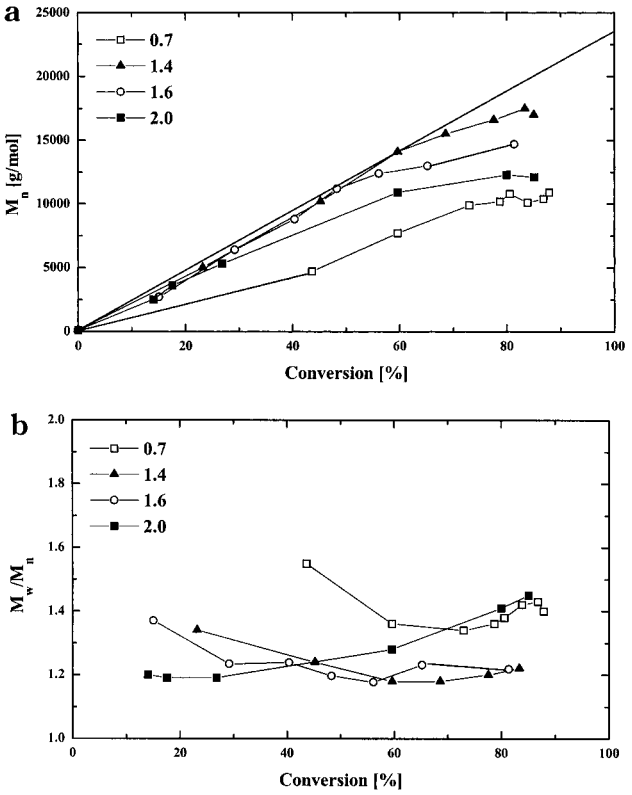

Figure 4. Oxazoline-terminated polystyrene. (a) Correlation of number-average molar mass M_n with conversion for [TEMPO]/[**OxaI**] ratios of 0.7, 1.4, 1.6, and 2.0; M_n(calcd) = 25 000 at 140 °C. (b) Correlation of polydispersities M_w/M_n with conversion for [TEMPO]/[**OxaI**] ratios of 0.7, 1.4, 1.6, and 2.0 at 140 °C.

stable radicals is higher than the number of formed radicals (at high [TEMPO]/[initiator] ratios) the polymerization slows down dramatically. This can be explained by the fact that the higher TEMPO concentration pushes the equilibrium between the active species and stable free radical and the adduct to the inactive form, decreasing the radical concentration. However as time proceeds, the radicals formed by autopolymerization readjust the relative radical concentrations, and the polymerization then proceeds. On the other hand, at low TEMPO concentration, conventional free-radical polymerization takes place. In the case of a bimolecular initiator, it is therefore important to determine the optimum [TEMPO]/[initiator] molar ratio in order to achieve a controlled polymerization.

Besides first-order kinetics, the dependence of molar mass on conversion and polydispersities are important features of controlled-radical polymerization. Figure 4 shows the plots for various [TEMPO]/[**OxaI**] ratios. It can be seen that the [TEMPO]/[initiator] molar ratio also affects the dependence of molar mass on conversion and polydispersities. Because the TEMPO concentration was held constant, the theoretical molar mass for 100% conversion can be calculated to be 25 000. Best linearity was achieved also for a ratio of 1.4 up to a conversion of 70%. At higher conversions, experimental molar mass was lower with respect to the calculated values. Most likely, thermal radical initiation of styrene polymerization occurs at high conversion, accompanied by a long polymerization time. This may result in active chains with low molar mass. Mechanistic studies showed thermal polymerization is essential for controlled-radical polymerization.[17] Polydispersities are displayed in

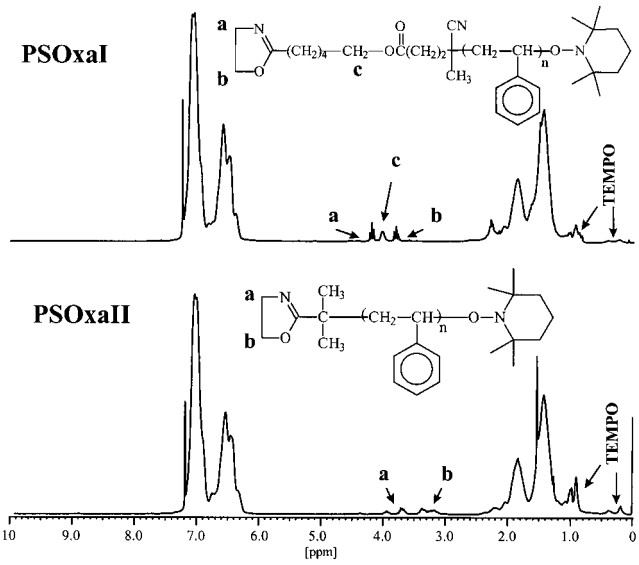

Figure 5. ^{1}H NMR-spectra in $CDCl_3$ for (a) **PSOxaI**, M_n(SEC) = 6000, and (b) **PSOxaII**, M_n(SEC) = 5000.

Figure 4b as a function of conversion. For [TEMPO]/[**OxaI**] molar ratios between 1.0 and 1.6 M_w/M_n, values of about 1.2 were found, whereas the polymerization with the molar ratio of 0.7 was associated with polydispersities of approximately 1.45 to 1.55. Low polydispersities were found at molar ratios of 2.0 at low conversions. However, at conversions exceeding 60%, the polydispersities increased above 1.5, which is due to the side reactions encountered at long reaction times. For further experiments, a [TEMPO]/[**OxaI**] molar ratio of 1.4 was chosen, because of low polydispersities, linear molar mass versus conversion dependence, and first-order kinetics up to high conversions.

The synthesized oxazoline-terminated polymers were characterized by SEC, and the oxazoline group was detected by NMR, FT-IR, and titration. To confirm that no residual initiator fragments were present, the polymers were reprecipitated three times. In Figure 5, ^{1}H NMR spectra of both polymers are shown. The ^{1}H NMR spectrum of **PSOxaI** shows the triplet peaks typical for oxazoline protons at 3.8 and 4.2 ppm. The spectrum of **PSOxaII** shows broad signals at 3.4 and 3.8 ppm, most likely due to broadening because of inhibited oxazoline ring rotation. Integration (taking into account aliphatic endgroup protons) of the molar mass can be calculated by determining the ratio of aliphatic to oxazoline protons. The C=N stretching band of the oxazoline group at 1675 and 1653 cm^{-1} for **OxaI** and **OxaII**, respectively, were detected by FT-IR. Again, molar mass was determined by integration of the oxazoline and a polystyrene band at 1943 cm^{-1} by calculating the ratio and calibrating it using SEC data. Moreover, endgroup functionality was measured by means of titration. Both the oxazoline and TEMPO endgroup are Lewis bases that can be protonated. By dissolving the polymer in equimolar amounts of THF and acetic acid, acetate anions are formed that can be titrated with $HClO_4$. By titration, the sum of TEMPO and oxazoline functionalities is detected, and molar mass is calculated by assuming a 1:1 molar ratio of TEMPO and oxazoline-based endgroups. In Figure 6, the values for molar mass calculated by endgroup determination (titration, NMR, and FT-IR) are compared to molar masses that were determined by SEC calibrated with polystyrene standards. For **PSOxaI**, good agreement of the molar

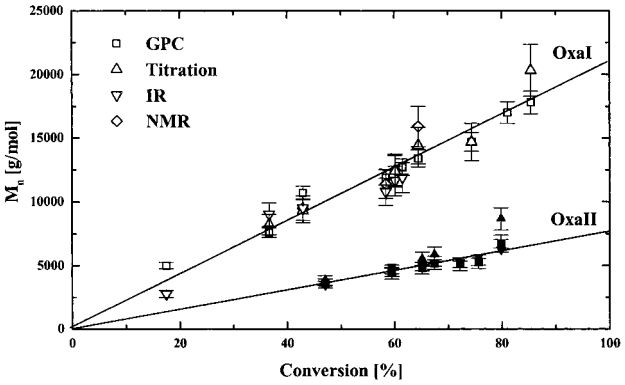

Figure 6. Determination of molar mass by SEC, endgroup determination by ^{1}H NMR, FT-IR and titration of the oxazoline and TEMPO endgroups, and polymerization at 140 °C for (a) **PSOxaI**, [TEMPO] = 0.036 mol/L and (b) **PSOxaII**, [TEMPO] = 0.091 mol/L.

masses determined by the different methods was found, thus confirming the presence of both oxazoline and TEMPO endgroups. In Table 1 M_n and M_w/M_n values and the degrees of functionality are listed for **PSOxaI**. The experimental errors of the endgroup determination methods were quantified in terms of bars in Figure 6. Deviations of functionalities are within the error limits of endgroup determination measurements (IR, NMR, and titration).

As can be seen in Table 2, **PSOxaII** shows within the error limits complete functionality up to high conversions regarding the oxazoline moiety. This was shown by FT-IR spectroscopy. In contrast, the degree of functionality determined by titration decreases gradually. Because the degree of functionality determined by FT-IR does not vary, this alteration must be due to a decreasing degree of TEMPO functionality. This is consistent with reports by Priddy et al. who showed that the TEMPO-based group decomposed to form hydroxylamines.[18] According to Priddy et al., at 140 °C for M_n = 10 000, at least 10% of chains lose their TEMPO functionality. He also showed that the effect is not as dramatic for the initiating radical side. In addition, Fukuda et al. demonstrated that the 10% decomposition time for PS-TEMPO in toluene at 140 °C is equal to about 1 h.[19] The difference of the degree of TEMPO functionality of **PSOxaI** compared to **PSOxaII** can be explained by the 3-fold higher TEMPO concentration of the TEMPO/**OxaII** styrene polymerization, yielding in longer reaction times. According to some reports,[17] thermal polymerization is essential for TEMPO-mediated polymerization. However, only a small fraction of the chains are induced thermally and the same amount recombines, leading to nonfunctionalized and difunctionalized polystyrene, respectively. Therefore, no important influence on molar mass, polydispersity and degree of functionality is observed.[17] As will be shown in the next chapter, the amount of dioxazoline-functionalized polystyrene is very small.

In conclusion, both oxazoline-functionalized azo initiators induce controlled-radical polymerization in the presence of TEMPO. It was shown that for conversion ranges from 0 to 80% with a [TEMPO]/[initiator] ratio of 1.4 for **OxaI** and 1.6 for **OxaII** first-order-kinetics, linear molar mass versus conversion dependence, and polydispersities below 1.3 were found. At conversion above 80%, i.e., longer reaction times, deviations occurred. Endgroup determination revealed molar masses which were in agreement with calculated values. It was shown that bimolecular initiators, such as TEMPO in conjunction with an azo initiator, afford controlled-radical polymerization and polymers with narrow polydispersities similar to those obtained with unimolecular initiators.

Reactivity of Oxazoline and Carboxylic Acid Endgroups of Polystyrene Synthesized by Controlled-Radical Polymerization. Novel mono(1,3-oxazolin-2-yl)-terminated polystyrene **PSOxaII** was applied as a component of the melt-phase coupling reaction with carboxylic acid-terminated polystyrene **CTPS** which was also produced by controlled-radical polymerization using biscarboxylic-functionalized azo initiators and TEMPO.[6] This coupling reaction of oxazoline-terminated polymers demonstrates the attractive potential of such intermediates in reactive processing and diversification of polymeric materials. Figure 7 shows the FT-IR spectrum of (a) **CTPS** (M_n = 6000) and (b) **PSOxaII** (M_n = 3600). The spectrum of **CTPS** shows the C=O stretching vibration of the monomeric carboxylic acid at 1751 cm^{-1} and the C=O stretching vibration of the dimer of the carboxylic acid at 1712 cm^{-1}.[20]

To obtain quantitative information on the reaction between oxazoline-terminated and carboxylic acid-terminated polystyrenes, a calibration curve was measured using low molar mass analogues. The scheme in Figure 8 shows the reaction between undecyloxazoline and phenylacetic acid to produce the corresponding ester amide. This ester amide is then mixed in different blend ratios with nonfunctionalized styrene homopolymer. Thus, it is possible to correlate the peak area of the amide I band at 1674 cm^{-1} directly with the content of ester amide in the sample. For internal calibration, the phenyl out-of-plane vibration at 1872 cm^{-1} of the styrene monomer unit is used. The calibration itself can be seen in Figure 8.

There exists a linear correlation between the number of amide groups per 100 styrene monomeric units and the integration value of the amide I band. The relative integration value is equal to the ratio of the integral of the amide I band and the phenyl out-of-plane vibration band of the styrene monomer unit. To obtain the conversion in percent, it is necessary to multiply the number of amide groups per 100 styrene units with the degree of polymerization of the respective polystyrene. Prior to FT-IR measurements, the reaction of oxazoline-terminated and carboxylic acid-terminated polystyrenes was detected by SEC, as shown in Figure 9.

A molar mass increase after the reaction between **PSOxaII** (M_n = 5800) and **CTPS** (M_n = 6000) can be observed after a reaction time of 60 min at 200 °C. The blend ratio was chosen in order to have equal molar amounts of the reactive endgroups. It can be seen that a bimodal molar mass distribution is obtained after 60 min at 200 °C. The SEC trace was fitted with two Pearson VII functions.[21] From the fit functions in Figure 9, it is possible to calculate the molar masses and the polydispersities of the two peaks separately. It results that the M_n value for the first peak is 6900 and for the second peak 16 200. The polydispersities are 1.23 and 1.27, respectively, and thus in accordance with those of functionalized polystyrenes reactants. The molar mass of the second peak is approximately twice that of the first peak (within the error limits of the SEC). Therefore, it can be assumed that the coupling of polystyrene after

Table 1. Determination of M_n and Degree of Functionality of PSOxaI

	M_n [g/mol]					degree of functionality [mol/kg]			
sample	SEC	titration[a]	IR[b]	NMR[c]	M_w/M_n	calcd	titration[a]	IR[b]	NMR[c]
PSOxaIA	7 600	8 200	9 000	n. d.[d]	1.21	0.132	0.122	0.111	n. d.
PSOxaIB	10 700	9 300	9 500	9 500	1.20	0.094	0.108	0.105	0.105
PSOxaIC	11 900	n. d.	10 800	11 400	1.23	0.084	n. d.	0.093	0.088
PSOxaID	12 500	12 400	11 600	12 500	1.26	0.080	0.081	0.086	0.080
PSOxaIE	13 400	14 400	12 500	15 900	1.27	0.075	0.070	0.080	0.063

[a] Determined by titration of oxazoline and TEMPO endgroup. [b] Determined by the oxazoline band at 1654 cm^{-1}. [c] Determined by NMR signal of oxazoline at 3.8 and 4.2. [d] Not determined.

Table 2. Determination of M_n and Degree of Functionality PSOxaII

	M_n [g/mol]				degree of functionality [mol/kg]		
sample	SEC	titration[a]	IR[b]	M_w/M_n	calcd	titration[a]	IR[b]
PSOxaIIA	3600	3800	3400	1.22	0.278	0.263	0.294
PSOxaIIB	4600	4400	4900	1.20	0.217	0.217	0.204
PSOxaIIC	4800	5500	5000	1.17	0.208	0.182	0.200
PSOxaIID	5200	5900	5200	1.15	0.192	0.169	0.192
PSOxaIIE	5100	n. d.[c]	5300	1.18	0.196	0157	0.189
PSOxaIIF	5300	n. d.	5700	1.19	0.189	n. d.	0.175
PSOxaIIG	6700	8700	6200	1.20	0.149	0.115	0.161

[a] Determined by titration of oxazoline and TEMPO endgroup. [b] Determined by the oxazoline band at 1654 cm^{-1}. [c] Not determined.

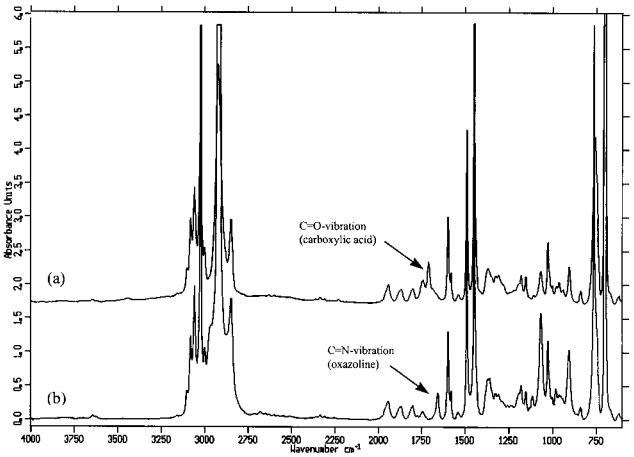

Figure 7. FT-IR spectra of (a) **CTPS** (M_n = 6000) and (b) **PSOxaII** (M_n = 3600).

reaction between the oxazoline-terminated and the carboxylic acid-terminated species is the main reaction. In addition, no peaks at higher molar masses are detected, which shows that the fraction of difunctionalized polystyrenes is very small. Now, it is possible to study the reaction kinetics employing FT-IR measurements. Figure 10a shows the FT-IR spectra in the range from 1630 to 1850 cm^{-1} of blends of **CTPS** and **PSOxaII** with equal molar amounts of reactive endgroups during the reaction at 200 °C for 60 min. The spectra are taken in time intervals of 1 min. Figure 10b shows the corresponding difference spectra, i.e., the normalized FT-IR spectrum at t = 0 min is always subtracted.

Clearly, the intensity of the C═N stretching vibration of the oxazoline at 1654 cm^{-1} and the carbonyl stretching vibration of the carboxylic acid at 1761 cm^{-1} decreased with increasing conversion, thus indicating endgroup conversion. There was simultaneous formation of an ester amide indicated by the growing peaks of the amide group with the amide I peak at 1675 cm^{-1} and the ester group with the carbonyl vibration at 1741 cm^{-1}. Isosbestic points at 1751, 1725, 1704, and 1660 cm^{-1} were observed. By using the calibration curve shown in Figure 8, it was thus possible to obtain the conversion as a function of time for the reaction of **CTPS** with **PSOxaII** having different molar masses. Figure 11 shows the kinetics plots for this reaction obtained by always using blend ratios of equal molar amounts of oxazoline and carboxylic acid groups at 200 °C, for **CTPS** with M_n = 6000 and **PSOxaII** with M_n = 3600, 4800, 5800, and 6700.

All reactions reached a plateau value at prolonged reaction times. The maximum conversion decreased with increasing molar mass. The conversion of **PSOxaII** and **CTPS** after a reaction time of 60 min was in agreement with the SEC data discussed above. Because the change of concentration with reaction time can be neglected in the range of the initial slope, the slope is proportional to the reaction rate constant. The reaction rate constant and the maximum conversion are listed in Table 3.

The average rate constant k for the reaction of **PSOxaII** and **CTPS** was determined to be 0.0128 L/mol and did not depend on molar mass or viscosity. The initial slope of the reaction shown in Figure 11 was different for the polystyrenes with different molar masses. However, the slower initial rate at higher molar mass is due to a lower overall concentration of reactive endgroups. At longer reaction times, maximum conversion is limited: the higher the molar mass, the lower the maximum conversion. We account this observation to a diffusion-controlled limit: with increasing molar mass, viscosity increases, and therefore, diffusion control appears at earlier conversions. An alternative explanation could be a deviation of functionalities at higher molar mass. However, IR measurements were not able to provide experimental evidence for such deviation (Table 2). The temperature dependence of the reaction was studied for the example of **PSOxaII** (M_n = 4800) mixed with **CTPS** (M_n = 6000) again for equal molar amounts of reactive endgroups. As is apparent in Figure 12, the temperature dependence of the reaction rate during the initial reaction can be described by an Arrhenius behavior. The activation energy of this reaction was calculated to be 65 kJ mol^{-1}.

Conclusion

New bis(1,3-oxazoline-2-yl)-functionalized azo initiators were synthesized, and their half-lives were deter-

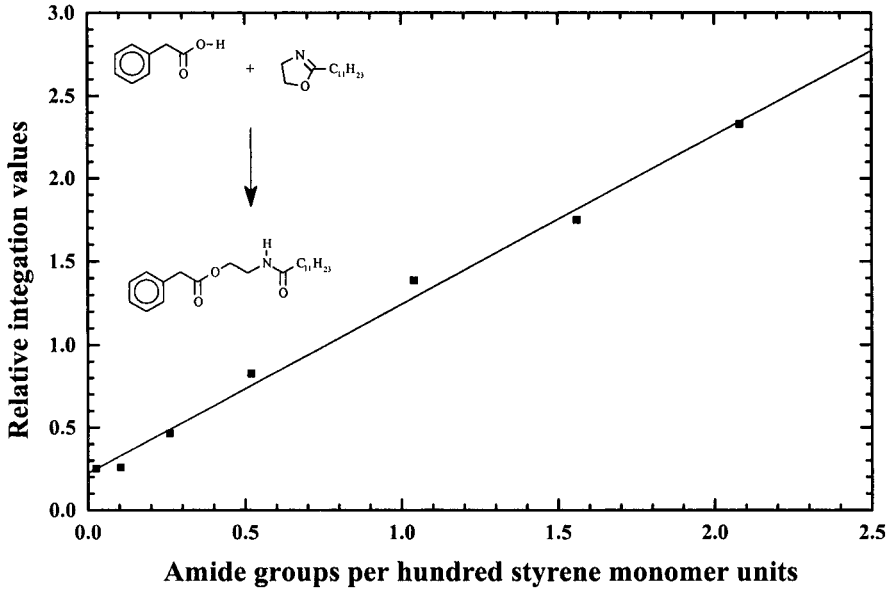

Figure 8. Calibration curve for the determination of the number of amide groups per 100 styrene monomer units obtained by mixing polystyrene with the reaction product shown in the scheme.

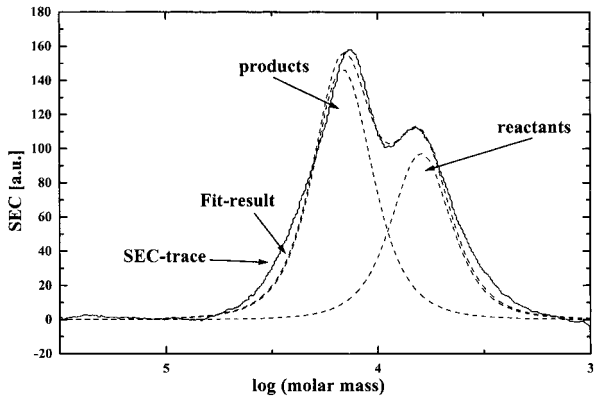

Figure 9. SEC trace of a blend of **PSOxaII** (M_n = 5800) and **CTPS** (M_n = 6000) after a reaction at 200 °C for 60 min. The blend contains equal molar amounts of carboxylic and oxazoline groups, respectively.

mined by UV spectroscopy. By using TEMPO and these functionalized initiators in conjunction with styrene at 140 °C, novel well-defined monooxazoline-terminated polystyrenes were obtained. The polymerization kinetics, molar mass versus conversion dependence, and polydispersities were examined with varying [TEMPO]/[initiator] molar ratios. Ideal controlled-radical polymerization behavior was found at [TEMPO]/[initiator] molar ratios of 1.4 and 1.6 for **OxaI** and **OxaII**, respectively. The degree of endgroup functionalites were determined by NMR, FT-IR, endgroup titration, and SEC data, revealing a complete functionality of the oxazoline endgroup and a decreasing TEMPO-based functionality with increasing polymerization time. The reactivity of the oxazoline functionality was proven by reacting monooxazoline- with monocarboxy-terminated polystyrene in melt without solvent (both polymers were synthesized by controlled-radical polymerization). According to FT-IR monitoring of the ester amide formation, resulting from coupling of oxazoline and carboxylic acid endgroups, maximum conversion is dependent upon molar mass. Endgroup conversion increased with decreasing polystyrene molar mass and reached a maximum of 70%. By shearing or using a solvent, this maximum might be increased. Another approach to

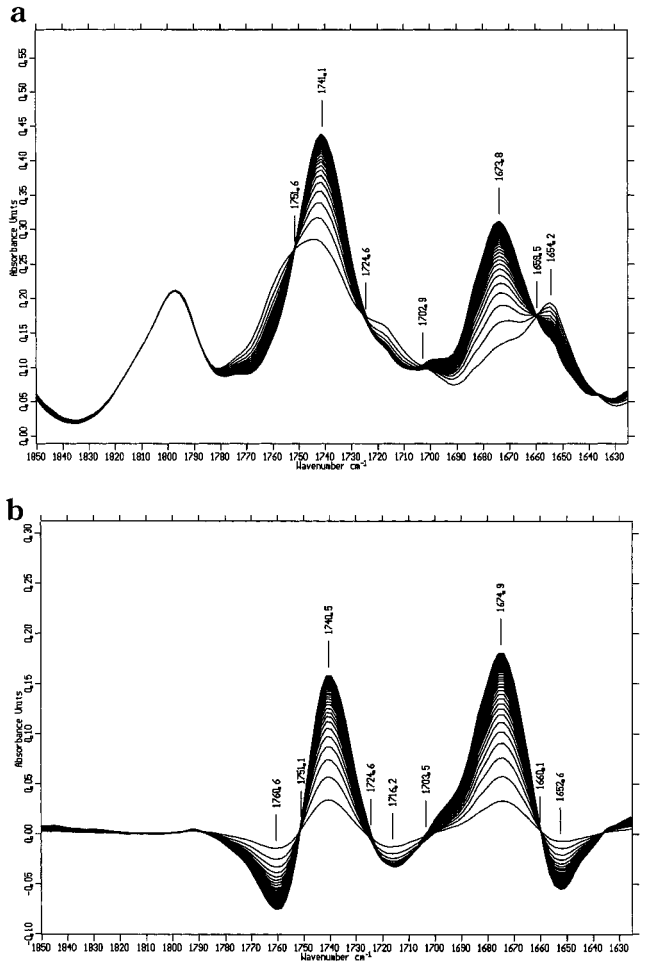

Figure 10. Reaction of **CTPS** (M_n = 6000) and **PSOxaII** (M_n = 3600) at 200 °C in intervals of 1 min. (a) FT-IR spectra. (b) Difference spectra.

higher conversions is an increase in the oxazoline reactivity by variation of the substituent in 2-position of the oxazoline ring.[13] Rate constants of this coupling reaction do not vary with molar masses, and the activation energy for the system **CTPS** (M_n = 6000)/**PSOxaII** (M_n = 4800) was measured to be 65 kJ/mol.

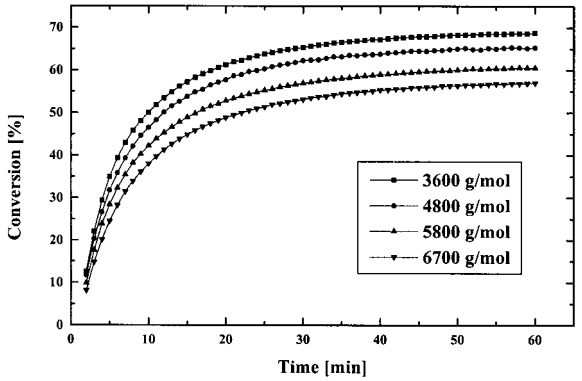

Figure 11. Conversion vs time plots for blends of **CTPS** with **PSOxaII** of different molar masses. Equal molar amounts of reactive endgroups were used, and the reaction temperature was 200 °C.

Table 3. Reaction Rate Constants and Conversion of the Reaction of CTPS (M_n = 6000) and PSOxaII with Varying Molar Mass[a]

molar mass of **PSOxaII**[b]	k (L/mol)[c]	conversion (%)[d]
3 600	0.0128	68
4 800	0.0129	65
5 800	0.0133	60
6 700	0.0122	57

[a] Determined after 60 min at 200 °C. [b] Determined by SEC. [c] Determined from the initial slope of conversion vs time plot. [d] Determined by calibration curve.

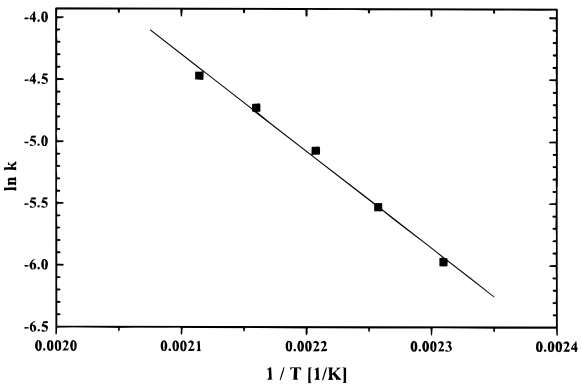

Figure 12. Arrhenius plot for the reaction of **PSOxaII** (M_n = 4800) with **CTPS** (M_n = 6000).

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(21) The Pearson VII function is a peak function with 4 parameters (A = peak area; m = profile shape factor; w = width; x_c = center). By varying the parameters a Gaussian or a Lorentz fit can be obtained.

$$y = A\frac{2\sqrt{m}\Gamma(2^{1/m}-1)}{\pi\Gamma(m-{}^1/_2)w}\left[1+4\frac{2^{1/m}-1}{w^2}(x-x_c)^2\right]^{-m}$$

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