Quasiliving cationic ring-opening polymerization of 2-ethyl-2-oxazoline in benzotrifluoride, as an alternative reaction medium

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Quasiliving cationic ring-opening polymerization of 2-ethyl-2-oxazoline in benzotrifluoride, an environmentally benign solvent

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Abstract

Cationic ring-opening polymerization (CROP) of 2-ethyl-2-oxazoline (EtOx) was systematically investigated in an environmentally benign solvent benzotrifluoride (BTF) simultaneously with conventional polymerization solvents, such as acetonitrile, N,N-dimethylacetamide and toluene, in the 80-100 °C temperature range. Kinetic experiments revealed that the monomer consumption occurs by first order kinetics and the number average molecular weights linearly increase in line with the theoretical molecular weight as a function of monomer conversion. These findings indicate that the polymerization takes place by quasiliving CROP in all the investigated solvents, including BTF as well. The highest polymerization rates were obtained in BTF, resulting in high conversions in short reaction times at 100 °C reaction temperature. The Arrhenius parameters of the polymerization of EtOx in BTF indicates relatively high activation energy in comparison with other applied solvents, however, a compensation effect between the activation energies and frequency factor is observed for such polymerization in a variety of solvents. Our findings are expected to enable the convenient synthesis of polyoxazolines and polyoxazoline-based well-defined polymer architectures in benzotrifluoride, an environmentally advantageous alternative solvent to harmful polymerization media, with high polymerization rates in short reaction times without the need for any special conditions or equipment.

Keywords: polyoxazoline, cationic ring-opening polymerization, quasiliving polymerization, benzotrifluoride, environmentally advantageous

1. Introduction

Polyoxazolines (POXs) have gained considerable interest in the last couple of years, due mainly to their various advantageous properties and application possibilities (see e.g. Refs. 1-42 and references therein). For obtaining POXs, cationic ring-opening polymerization (CROP) of 2-substituted-2-oxalines, especially CROPs proceeding by the quasiliving manner, i.e. via dynamic equilibrium between propagating (living) and nonpropagating (non-living), but reactive, polymer chains in the absence of irreversible chain breaking reactions (termination and/or chain transfer) [43], is the most preferred process (see e.g. 2-11,17-20,25-29,33 and references therein). The quasiliving CROPs (QL-CROP), displayed in Scheme 1, enable the synthesis of a wide range of tailor-made polymers and well-defined macromolecular assemblies, such as functional POXs, random and block copolymers, and polymers with various topologies by the variation and manipulation of functional groups derived from the initiator, monomer or terminating agents [2-7,16,17,22,35,36]. The most widely used initiators are alkylating agents such as alkyl/aryl/acetyl halides, tosylates (methyl p-toluenesulfonate) and triflates (trifluoromethanesulfonate) [8]. Triflates show higher reactivity over tosylates, but due to their inherent instability, nosylates (p-nitrobenzenesulfonate) were found also to be an effective alternative [9]. Chain end functionalities can be introduced into POXs by either using functional initiators or terminating agents, or both [2-6,23,24,35,36]. In the course of the QL-CROP process, the rate of polymerization will depend on the reactivity of the cationic species and the rates of the equilibrium reactions between the propagating (living) chain and the covalent (nonpropagating, non-living) polymer chains (Scheme 1). The rates of these elementary reactions of the QL-CROP process will depend on the counter ion derived from the initiator, the monomer, reaction temperature and solvent. In general, the equilibrium between the cationic and covalent species is shifted toward the propagating oxazolinium ion with

increasing solvent polarity, which leads to higher polymerization rates [4]. So far, several solvents, such as acetonitrile [9-22], butyronitrile [13,23], chlorobenzene [10,14,21], chloroform [24], dichloromethane [25], dimethylacetamide [8,10,26-28], ionic liquid [29], nitrobenzene [18], nitromethane [30], and sulfolane [10,31,32] have been reported as polymerization media for the CROP of 2-oxazolines. Up to now, acetonitrile is far the most common solvent used for oxazoline polymerization. However, the relatively slow polymerization rates in this solvent and its toxicity have raised the need for alternatives. In a recent study [33], ethyl acetate as a green alternative solvent was reported for the polymerization of 2-ethyl-2-oxazoline. The drawbacks of ethyl acetate relate to the relatively low polymerization rates at lower temperatures than its boiling point of 77 °C, and thus to the need for special equipment for polymerizations at higher temperatures. Furthermore, the good miscibility of ethyl acetate with water may lead to environmental problems, especially by the presence of unreacted substances in this solvent. To overcome the relatively low polymerization rates in most of the applied solvents, sulfolane was found as rate accelerating solvent for the CROP of 2-oxazolines [10]. However, the degradability of this solvent to acidic species may restrict its broad range of application for CROP of oxazolines.

Benzotrifluoride (BFT) (or α,α,α-trifluorotoluene, TFT), a trifluorinated derivative of toluene, is considered as one of the solvents with environmentally advantageous characteristics. Its polarity is similar to dichloromethane (DCM), but BTF has a significantly higher boiling point of 102 °C. Due to the high stability of the trifluoromethyl group in BTF, linked to the aromatic ring, even at elevated temperatures, the commercial availability, the low volatility, and low toxicity, BTF is obviously a robust and suitable choice as an alternative solvent for the replacement of aromatic (benzene, toluene, xylene) and halogenated compounds (dichloromethane, chloroform) [44]. It has been already applied as an alternative solvent for various organic synthetic reactions previously conducted in dichloromethane,

toluene or nitrobenzene [44-48]. In addition, BTF proved to be an appropriate solvent for a variety of polymerization reactions as well. Obviously, it is a suitable medium for the polymerization of various fluorous or semifluorous monomers [49,50], on the one hand. On the other hand, BTF was reported to be applied for the cationic polymerization of β-pinene [51], isoprene [52], styrene [53] and isobutylene [54]. The quasiliving ATRP of styrene and n-butyl acrylate in BTF was also successfully carried out in this solvent [55]. However, to the best of our knowledge, there are no systematic investigations so far dealing with the use of BTF as solvent for oxazoline polymerizations, although BTF can be taken into account as a promising alternative medium for the CROP of oxazolines at relatively high temperatures, and replace the conventionally applied more hazardous solvents, such as acetonitrile, chlorobenzene, nitrobenzene and dimethylacetamide.

In a recent study, it was found by us that BTF is a suitable common solvent for poly(2-ethyl-2-oxazoline) (PEtOx) and the highly hydrophobic polyisobutylene (PIB) for the preparation of thermoresponsive PIB-PEtOx block copolymers with an internal ionic liquid moiety [35]. Inspired by this finding, we have become interested to carry out systematic investigations on the CROP of 2-ethyl-2-oxazoline (EtOx) in BTF in order to reveal the characteristics of this polymerization in this environmentally benign solvent at temperatures in the range of 80-100 °C. Methyl tosylate (MeOTs) was selected as initiator which ensures fast initiation. Kinetic experiments were conducted in order to determine the rate of polymerization not only in BTF, but for reason of comparison also in acetonitrile, toluene and N,N-dimethylacetamide (DMAc). Herein, we report on the results of these investigations, which enable to open new possibilities for applying BTF as an environmentally benign solvent for convenient polymerizations of oxazolines, and thus for the preparation of novel polyoxazoline-based macromolecular assemblies by utilizing our current findings and the solubility advantages offered by benzotrifluoride.
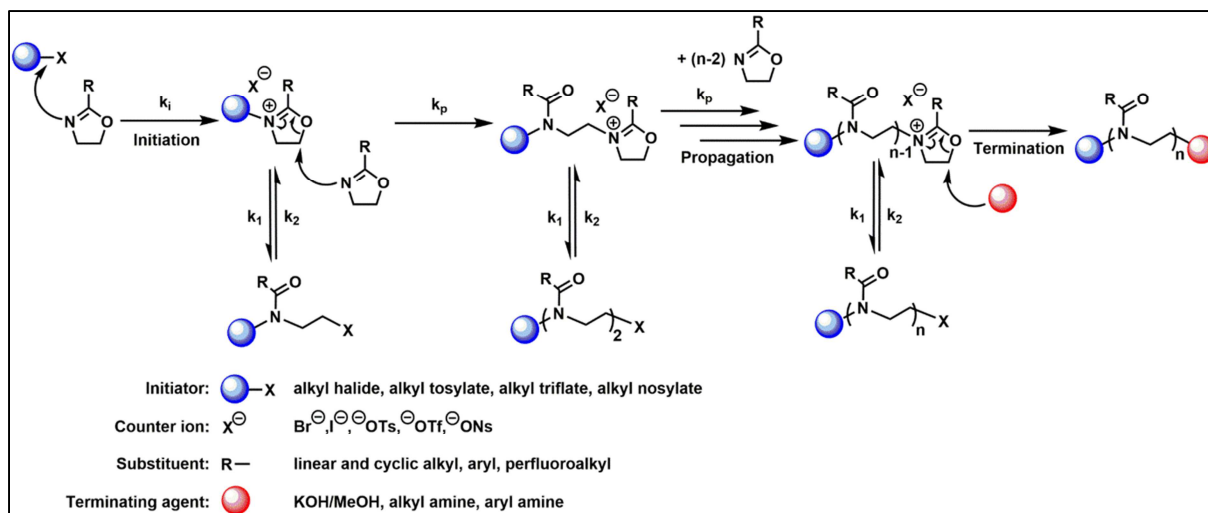
Scheme 1. The elementary processes of the quasiliving cationic ring-opening polymerization of 2-oxazolines.

2. Experimental

2.1. Materials

Methyl tosylate (MeOTs, 98%, Aldrich) was purified by recrystallization from diethyl ether yielding a completely white, clear solid, and was stored at 4 °C under dry nitrogen atmosphere. Benzotrifluoride (BTF, anhydrous, ≥99%, Sigma-Aldrich), 2-ethyl-2-oxazoline (99+%, Aldrich), acetonitrile (Reanal), dimethylacetamide (DMAc, 99.8%, Sigma-Aldrich), and toluene (≥99%, Molar Chemicals) were refluxed and distilled over CaH_2 and stored under dry nitrogen atmosphere until use at 4 °C.

2.2. Characterization

^{1}H NMR spectroscopic measurements were performed on a Varian or Bruker 500 MHz spectrometer using $CDCl_3$ as solvent. For the spectra calibration of the ^{1}H NMR spectra, the chloroform peak was set to 7.26 ppm.

Gelpermeation chromatography (GPC) measurements of PEtOx were performed on an Agilent 1260 Infinity equipment equipped with PSS Gram 30 Å and 1000 Å polyester

copyright network columns in DMAc/LiBr (0.5 wt%) eluent, with 1 ml/min flow rate at 50 °C. The average molecular weights were determined on the basis of calibration with PMMA standards.

2.3. Polymerization of 2-ethyl-2-oxazoline in different solvents

2-Ethyl-2-oxazoline (4.07 ml, 4.00 g, 0.0404 mol, 100 eq.) and 2 ml of dry solvent (BTF/acetonitrile/toluene/DMAc) was charged in a previously flame-dried and degassed Schlenk flask. With constant stirring, the initiator stock solution (2 ml) of methyl tosylate (0.075 g, 0.0004 mol, 1 eq.), dissolved in the applied solvent, was carefully added. Then the reaction mixture was immersed in an oil bath preheated to the desired temperature (80/90/100 °C), and stirred until a predetermined period of time. For determination of the monomer conversion and analysis of the resulting polymers, 0.8 ml amount of samples were withdrawn at given reaction times for ^{1}H NMR and GPC analyses. The withdrawn samples were precipitated by dropwise addition into tenfold excess of diethyl ether, then the products were filtered off, washed by diethyl ether and dried under vacuum at room temperature until constant weight.

3. Results and Discussion

In order to reveal the influence of BTF, together with other solvents for comparison, such as acetonitrile, DMAc and toluene, on the CROP of EtOx initiated by MeOTs, systematic polymerization experiments were carried out in the temperature range of 80-100 °C. The solubility of PEtOx (MW = 10000 g/mol) was tested in these solvents in advance, and all of them was found to be good solvents for this polymer. PEtOx readily dissolved in BTF, acetonitrile and DMAc, while with a slower rate, but completely, in toluene at room temperature. The EtOx monomer was found to be miscible with all these solvents. Table 1

shows that acetonitrile, which is widely used as reaction medium for oxazoline polymerizations, has the highest dipole moment and polarity, but the lowest boiling point of 82 °C among the investigated solvents. The dipole moment and polarity of N,N-dimethylacetamide (DMAc) is somewhat lower than that of acetonitrile, but higher than that of BTF. Toluene is the less polar among the investigated solvents.

Table 1. The boiling points, dipole moments and polarities of the applied solvents.

Solvent	Boiling point (°C)	Dipole moment	Polarity
Benzotrifluoride	102	2.86	0.241
Acetonitrile	82	3.92	0.460
Toluene	111	0.36	0.099
DMAc	166	3.72	0.377

A series of kinetic experiments was performed for the CROP of EtOx with relatively high monomer concentrations ($[M]_0$=5.05 mol/dm^3) and with a target DP_n of 100. Figure 1 (left) shows the first order kinetic plots of the conversion of EtOx, determined by ^{1}H NMR spectroscopy, in the investigated solvents at 80, 90 and 100 °C (see Figure S1 for a series of ^{1}H NMR spectra as a function of reaction time in the Supporting Information). As displayed in these first order plots, the data points fall on a straight line, that is the consumption of EtOx occurs by first order kinetics in these CROPs in all the examined solvents, including BTF as well. This indicates that permanent termination does not take place in the investigated solvents in the applied temperature range. Due to the boiling point of acetonitrile of 82 °C, the EtOx polymerization was carried out only at 80 °C with this solvent. It is evident from the first order plots that these polymerizations proceed with significantly higher rates in BTF than in all the other solvents, and high yields are obtained in this solvent at 100 °C reaction

temperature in a short time, i.e. in about an hour. It is also noteworthy to mention that the overall polymerization rates are higher in the less polar toluene than in DMAc with significantly higher polarity, but less than in BTF, its structural counterparts. These results indicate that solvent polarity is not exclusively determine the polymerization rates in ionic polymerizations, such as CROP of oxazolines.

In the course of these experiments, all samples were isolated and purified, and were analyzed by GPC to gain information on the molecular weight distribution (MWD) and average molecular weights of the PEtOx obtained by the investigated polymerizations (see the GPC curves in Figures 1 and S2-S9). It is evident from these Figures that the GPC curves are shifted towards lower elution volumes, i.e. towards higher molecular weights with increasing reaction times. This can be attributed to the chain growth of all the chains in the course of these polymerizations. Indeed, as shown in Figure 1 (right), the M_n values of the resulting polymers are in good correlation with the theoretical line, and there is a linear increase in the average molecular weights as a function of monomer conversion. Since the theoretical M_n versus conversion lines were constructed by assuming living polymerization with 100% initiating efficiencies, it can be concluded that the MeOTs initiator is consumed fast at the beginning of these polymerizations with nearly quantitative, i.e. close to 100% initiating efficiencies. On the basis of these results, it can be concluded that MeOTs acts as an effective initiator for the CROP of EtOx in all the investigated solvents, including BTF as well, in the 80-100 °C temperature range. Evidently, the linear first order plots and the nearly theoretical M_n values of the resulting PEtOx samples indicate that permanent termination or chain transfer reactions do not occur in the polymerization of EtOx in the solvents used as reaction media. This means that all these CROPs of EtOx proceed according to the mechanism depicted in Scheme 1, i.e. by quasiliving CROP not only in the solvents used already in EtOx polymerizations earlier, but in BTF as well. The PEtOxs synthesized in BTF, acetonitrile and

toluene have relatively narrow MWDs with polydispersities of 1.3-1.5, which is similar to previously reported results for the CROP of EtOx in acetonitrile [11]. The polymers synthesized in DMAc have a bit broader MWDs, and thus higher polydispersities of 1.5-1.9. These findings indicate that BTF is a useful solvent to carry out quasiliving CROP of oxazolines with well-defined average molecular weights and relatively narrow molecular weight distributions.
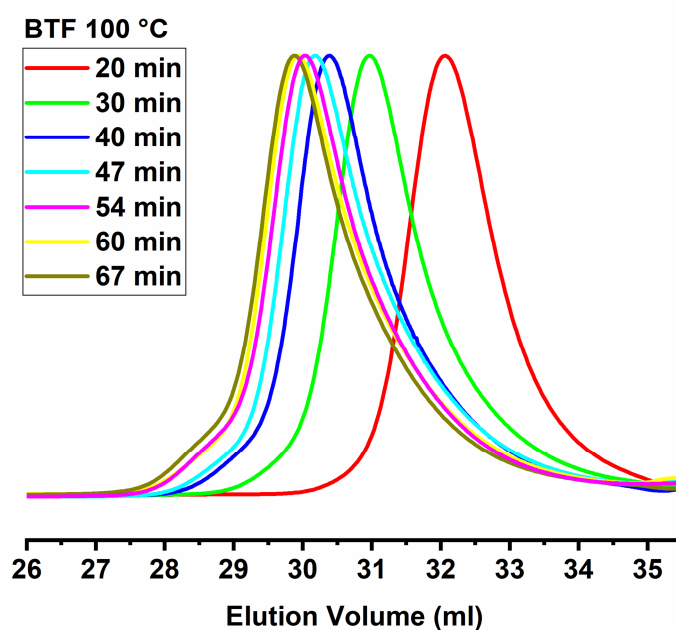

Figure 1. GPC curves of PEtOx samples obtained in benzotrifluoride as polymerization medium at 100 °C at different polymerization reaction times.
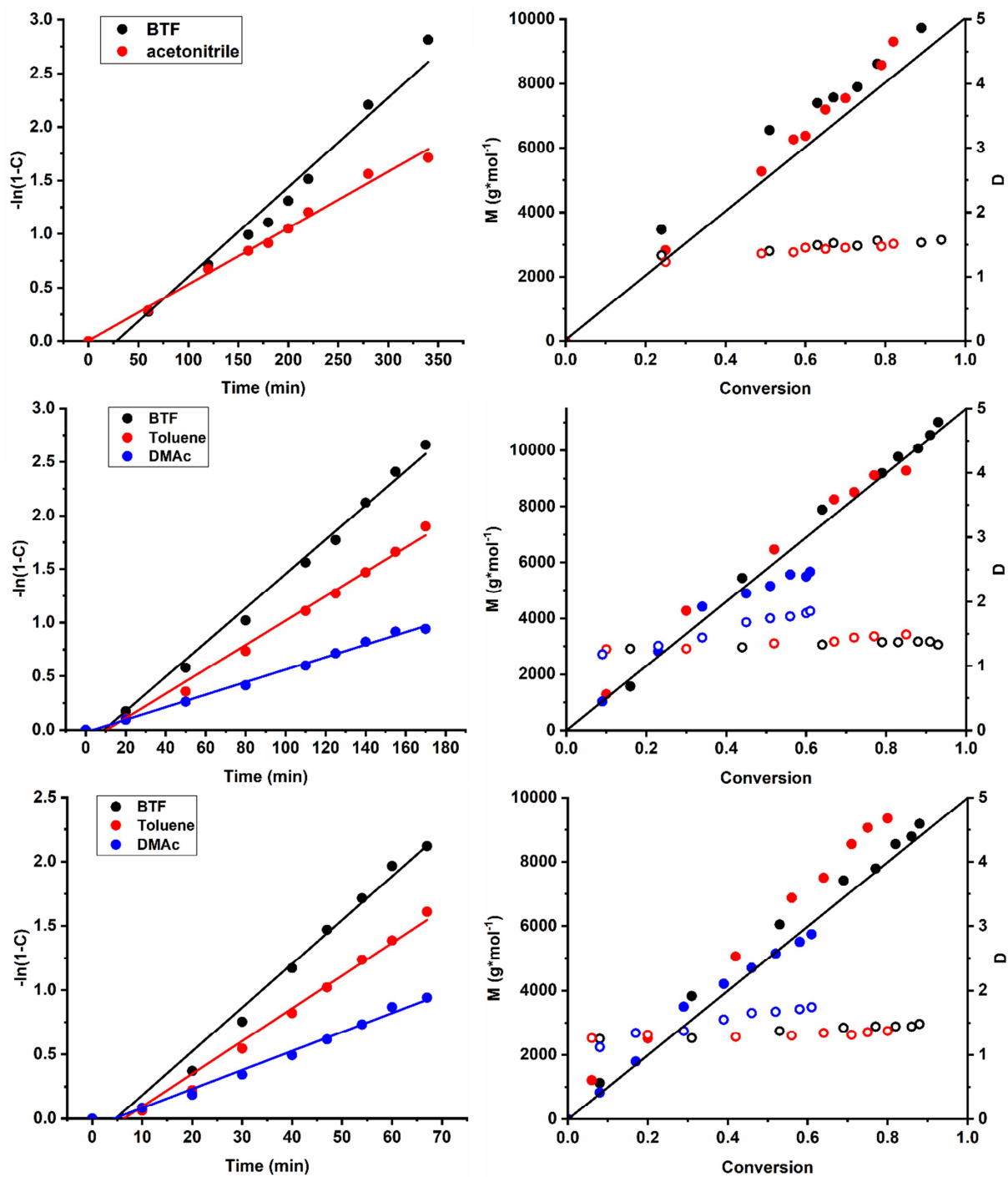
Figure 2. The first order plots of the monomer conversions (C) obtained by the CROP of EtOx initiated by MeOTs (left), and the number average molecular weights (●) and polydispersities (○) as a function of monomer conversion in different solvents at different temperatures (right) (T = 80 °C (top), 90 °C (middle), 100 °C (bottom); $[M]_0$=5.05 mol/dm^3; $[M]_0/[I]_0$=100).

Table 2. The polymerization rate constants (k_p) of the cationic ring-opening polymerization of EtOx in BTF, acetonitrile, toluene and N,N-dimethylacetamide (DMAc) at different temperatures ([EtOx] = 5.05 mol/dm^3, [MeOTs] = 0.05 mol/dm^3).

Solvent	T (°C)	$k_p \cdot 10^3$ (dm^{3}mol^{-1}s^{-1})
BTF	80	2.76
Acetonitrile	80	1.74
BTF	90	5.28
Toluene	90	3.75
DMAc	90	1.92
BTF	100	11.24
Toluene	100	8.40
DMAc	100	4.87

The apparent polymerization rate constants (k_p) were determined from the slopes of the first order plots in Figure 2 and are shown in Table 2. As the data clearly indicate in Table 2, the rate constant of the polymerization of EtOx is remarkably higher in BTF than in the conventionally applied acetonitrile, toluene and DMAc at all examined polymerization temperatures. The apparent polymerization rate constant of the EtOx polymerization in BTF at 100 °C ($k_p = 11.24 \cdot 10^{-3}$ dm^{-3}mol^{-1}s^{-1}) is in the range of rate constants reported for the commonly used acetonitrile ($k_p = 9.91 \cdot 10^{-3}$ dm^{-3}mol^{-1}s^{-1}) [11] and the recently described ethyl acetate ($k_p = 11.6 \cdot 10^{-3}$ dm^{-3}mol^{-1}s^{-1}) [33] as solvents for EtOx polymerizations. However, acetonitrile and ethyl acetate have boiling points of 82 °C and 77 °C, respectively. Therefore, these volatile and water-miscible solvents, which thus provide potential environmental hazards, require special, pressure-safe polymerization reactors at higher temperatures than that of their boiling points. In contrast, polymerization of EtOx can be conveniently carried out in BTF having low toxicity, low water miscibility, low volatility and boiling point of 102 °C, which also provides possibility for polymerizations in refluxing BTF, i.e. without additional heating and temperature regulation. Thus, it can be concluded that these results clearly identify BTF as a new alternative and environmentally advantageous polymerization

solvent for the quasiliving CROP of EtOx with higher polymerization rates than that in the conventionally used acetonitrile. Moreover, its higher boiling point facilitates the use of BTF at even higher reaction temperatures without the need of any special equipment or technique for obtaining PEtOx with high yields in short reaction times, predetermined molecular weight and narrow molecular weight distribution.

Table 3. The Arrhenius parameters of the cationic ring-opening polymerization of 2-ethyl-2-oxazoline in different solvents.

Solvent	E_A (kJ/mol)	$A \cdot 10^{-8}$ (s^{-1})	Reference
BTF	76.9	6.29	this work
Acetonitrile	73.4	1.99	11,20
Ethyl acetate	70.7	0.89	33
DMAc	68.7	0.1*	27
sulfolane	74.3	4.80	10

*Estimated from the data in Ref. 2

The Arrhenius plot (Figure S10) of the rate constants of EtOx polymerization obtained in BTF provides an overall activation energy of 76.9 kJ/mol and frequency factor of $6.29 \cdot 10^8$ s^{-1}. Both the activation energy and the frequency factor are higher in BTF than the previously reported literature values for the CROP of EtOx in other solvents as shown in Table 3. It is interesting to note that the dipole moment and polarity data of the solvents (Table 1) do not indicate correlation between the Arrhenius parameters with the solvent parameter values, i.e. it is likely that the apparent polymerization rate originates from the dependence of the rate constants of the elementary events, that is, that of the equilibrium reactions and propagation, according to the mechanism of the quasiliving CROP as shown in Scheme 1. It is interesting to note that the available Arrhenius parameters show remarkable compensation effect, meaning that higher the activation energy, higher the frequency factor.

4. Conclusions

Systematic cationic ring-opening polymerization (CROP) of 2-ethyl-2-oxazoline (EtOx) was carried out in an environmentally benign solvent, benzotrifluoride (BTF) possessing low toxicity, low volatility and low water-miscibility, in comparison with solvents conventionally used for such reactions, such as acetonitrile, N,N-dimethylacetamide and toluene. Due to its appropriate polarity and conveniently high boiling point (102 °C), BTF is an attractive solvent candidate for several type of organic syntheses and also for polymerization processes. The results of the kinetic investigations of this work show that the polymerization of EtOx proceeds via quasiliving polymerization without detectable irreversible chain breaking reactions in all the investigated solvents, including BTF as well. The polymerization of EtOx takes place with significantly higher rates in BTF than in the conventional solvents. Thus high polymerization yields are obtained without any special equipment at convenient polymerization temperatures (100 °C) in short times. These results indicate that BTF can be efficiently utilized for oxazoline polymerizations, and as a consequence, for the preparation of various novel macromolecular structures due to its suitability as cosolvent for polyoxazolines and various other polymers.

Appendix A.

Supplementary data. Supplementary data to this article can be found online at …

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