Effect of Solvent on the Activation Rate Parameters for Polystyrene and Poly(butyl acrylate) Macroinitiators in Atom Transfer Radical Polymerization

Grégory Chambard, Bert Klumperman,* and Anton L. German

Laboratory of Polymer Chemistry, Department of Chemical Engineering & Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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ABSTRACT: The activation rate parameters of polystyrene (k^{S}_{act}) and poly(butyl acrylate) (k^{BA}_{act}) macroinitiators in ATRP catalyzed by CuBr/4,4′-di-*n*-heptyl-2,2′-bipyridine have been determined at 110 °C using a combination of nitroxide exchange reactions with HPLC analysis. The method is based on exchange of the bromide end group with a hydroxy-TEMPO end group. The depletion of the macroinitiator is monitored as a function of time. The method is applicable in different solvents, which implies the possibility to investigate the effect of solvent characteristics. Solvent polarity has a negative influence on k^{S}_{act} and a positive effect on k^{BA}_{act}. The ability of the solvent to act as ligand in the copper complex hampers the activation process for both macroinitiators, while the presence of hydroxy groups in the solvent increases both activation rate parameters.

Introduction

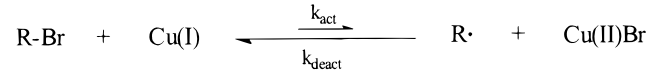
One of the most convenient ways to produce polymer materials on an industrial scale is via free-radical polymerization.[1] A wide range of monomers is polymerizable, and virtually any combination of monomers can be copolymerized. In contrast to living polymerizations such as anionic[2] and group transfer polymerizations,[3] polymer architecture and microstructure are not controllable in free-radical polymerizations. In the past decade, controlled radical polymerizations have been developed that combine the benefits of both free-radical and living polymerizations.[4−7] One of the most studied techniques is atom transfer radical polymerization (ATRP).[5,6] ATRP can be applied to a large variety of monomers[8−11] to produce polymers with well-defined microstructures.[12] The ATRP system relies on one equilibrium reaction in addition to the classical free-radical polymerization scheme (Scheme 1). In this equilibrium, a dormant species (R−Br) reacts with the activator (Cu(I)) to form a radical (R•) and a deactivating species (Cu(II)Br). The activation and deactivation rate parameters are k_{act} and k_{deact}, respectively. Since deactivation of the growing radicals is reversible, control over the molecular weight distribution and, in the case of copolymers, over chemical composition can be obtained if the equilibrium meets several requirements.[12,13]

1. The equilibrium constant, k_{act}/k_{deact}, must be low in order to maintain a low stationary concentration of radicals. A high value would result in a high stationary radical concentration, and as a result, termination would prevail over reversible deactivation.

2. The dynamics of the equilibrium must be fast; i.e. deactivation must be fast compared to propagation in order to ensure fast interchange of radicals in order to maintain a narrow molecular weight distribution.

Few copolymerizations have been published until now.[14−17] Matyjaszewski et al. investigated the bulk copolymerization of styrene and butyl acrylate from a kinetic point of view.[18] They reported a decreasing slope in the evolution of $-\ln(1 - \text{conversion})$ vs time and concluded that this was due to the change in monomer feed ratio. In their study, the monomer feed ratio changed due to composition drift from styrene-rich toward butyl acrylate-rich. Therefore, they ascribed the decreasing reaction rate to the increase in polarity of the reaction medium, which they speculated enhances the activation of styrene-end-capped dormant species. This would lead to an increase in the stationary radical concentration, resulting in more termination events and thus leading to a lower reaction rate.

Scheme 1. Equilibrium Reaction in ATRP



One of the most important parameters in ATRP is the activation rate parameter, k_{act}. Fukuda et al. introduced a simple method to determine this rate parameter experimentally using size exclusion chromatography (SEC).[19] In this method, the macroinitiator is added together with monomer, the copper complex, and a conventional free-radical initiator such as *tert*-butyl hydroperoxide. It is based on decreasing the rate of deactivation by the reaction of the radicals originating from the conventional free-radical initiator with the Cu(II)Br species. The transient lifetime of the radicals originating from the macroinitiator will therefore increase, and more monomer units are added. The decrease of the macroinitiator concentration can then be followed by SEC. To get good resolution in SEC, the amount of conventional free-radical initiator must be fine-tuned, which is a difficult and often impractical task. Furthermore, k_{act} can only be determined in the presence of a monomer, preferably a monomer with a high propagation rate constant, to ensure good peak separation in SEC. Very recently, Fukuda et al. reported a second method to determine activation rate parameters.[20] The method is based on a similar principle, i.e., the impediment of reversible deactivation by a reaction of the radical originating from the macroinitiator by a trapping agent. They used a stable free radical (2,2,6,6-dimethylpiperidine-*N*-oxyl or TEMPO) to monitor the decrease in concentration of the macroinitiator by means of NMR.

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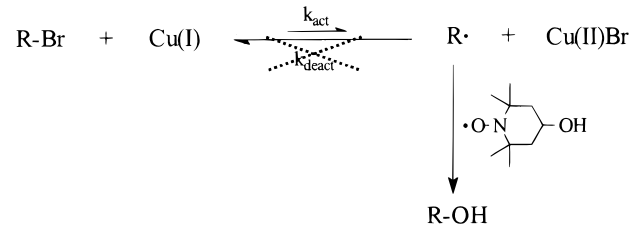
Scheme 2. Exchange Reactions with Hydroxy-TEMPO



Fundamental knowledge of the kinetic behavior of the ATRP system could be used to develop simple rules to predict ATRP copolymerization under different reaction conditions. This paper introduces a methodology to determine activation rate parameters of dormant species by combination of exchange reactions similar to the NMR method of Fukuda et al.[20] with subsequent analysis by HPLC. The applicability of the method in different solvents allows systematic investigations of the effect of solvent characteristics on the activation rate parameters in ATRP.

Method

Our method utilizes exchange experiments that are also the basis for determining the dissociation rate parameters of alkoxyamines.[21] The radicals originating from the macroinitiator are irreversibly trapped by a stable nitroxide radical to yield a hydroxy functional species, R−OH (Scheme 2). To obtain pseudo-first-order kinetics, the only fate of the radicals originating from the macroinitiator must be to be trapped by hydroxy-TEMPO with no transformation back to the dormant species. This can be achieved by utilizing a large excess of hydroxy-TEMPO. When pseudo-first-order kinetics apply, differential equation **(**1**)** applies.

$$-\frac{\mathrm{d}[\mathrm{R-Br}]}{\mathrm{d}t} = k_{\mathrm{act}}[\mathrm{R-Br}][\mathrm{Cu(I)}] \qquad (1)$$

The general solution for this differential equation is eq 2.[20] Note that the [Cu(I)] is not constant but decreases as well in the exchange reactions.

$$\ln\left(\frac{[\mathrm{R-Br}]_0}{[\mathrm{R-Br}]_t}\right) + \ln\left(\frac{[\mathrm{Cu(I)}]_0 - [\mathrm{R-Br}]_0 + [\mathrm{R-Br}]_t}{[\mathrm{Cu(I)}]_0}\right) = ([\mathrm{Cu(I)}]_0 - [\mathrm{R-Br}]_0)k_{\mathrm{act}}t \qquad (2)$$

The subscripts 0 and t denote concentrations at times 0 and t, respectively. Experimentally, the macroinitiator can be separated from the hydroxy functional product by quantitative HPLC. Therefore, the decrease in the concentration of dormant species can be monitored as a function of time. When the left-hand side of **(**2**)** is plotted vs time, a linear relationship is obtained whose slope corresponds to $([\mathrm{Cu(I)}]_0 - [\mathrm{R-Br}]_0)k_{\mathrm{act}}$.

Experimental Section

Materials. The copper ligand, 4,4′-di-*n*-heptyl-2,2′-bipyridine (dHbpy), was synthesized by a literature procedure.[22] Styrene (S, Aldrich, 99%) and butyl acrylate (BA, Aldrich, 99+%) were distilled and stored over molecular sieves. *p*-Xylene (Aldrich, 99+% HPLC grade) and dry *N*,*N*-dimethylformamide (DMF, Biosolve, 99.8%) were stored over molecular sieves and used without further purification. Butyl acetate (BuAc, Merck, 99+%), dioxane (Biosolve, 99.8%), and 1-butanol (Aldrich, 99.8% HPLC grade) were used as received. CuBr (Aldrich, 98%), ethyl 2-bromoisobutyrate (Aldrich, 98%), and hydroxy-TEMPO (Aldrich) were used without further purification.

Macroinitiator Synthesis. Polystyrene (PS−Br) and poly(butyl acrylate) (PBA−Br) macroinitiators were synthesized with ATRP. Xylene (10.0 g), monomer (10.0 g of S or 12.3 g of BA, 0.0960 mol), ethyl 2-bromoisobutyrate (0.624 g, 3.20×10^{-3} mol), and dHbpy (0.549 g, 1.56×10^{-3} mol) were mixed in a 100 mL round-bottom flask. The mixture was then purged with argon for 30 min, after which CuBr (0.112 g, 7.81×10^{-4} mol) was added. The reaction mixture was then homogenized and purged with argon for another 30 min, after which the reaction mixture was heated to 110 °C. After a time period, the reaction mixture was quenched and passed through a column with activated alumina. The molecular weights of both macroinitiators were measured by SEC calibrated with polystyrene standards with narrow molecular weight distributions (Polymer Laboratories) and, in the case of PBA−Br, corrected with Mark−Houwink parameters[23] and were 1585 g/mol for PS−Br ($M_w/M_n = 1.08$) and 2300 g/mol for PBA−Br ($M_w/M_n = 1.16$).

Exchange Reactions. Exchange reactions were carried out in xylene, dioxane, butyl acetate, 1-butanol, and DMF. A typical procedure for an exchange reaction with PS−Br in xylene is as follows. Xylene (10 mL), hydroxy-TEMPO (0.172 g, 1.00×10^{-3} mol), dHbpy (0.141 g, 4.01×10^{-4} mol), and PS−Br (0.0792 g, 5.00×10^{-5} mol) were mixed in a 100 mL round-bottom flask. The mixture was then degassed by purging with argon for at least 30 min, after which CuBr (0.0287 g, 2.00×10^{-4} mol) was added. The reaction mixture was then homogenized and purged with argon for another 15 min. After this time period, the reaction mixture was instantaneously heated to 110 °C, and in time samples were taken through a septum.

HPLC Measurements. Prior to analysis, the samples from the exchange experiments were passed through a column of activated alumina, after which they were subjected to drying. The samples were then dissolved in CH_2Cl_2 (Aldrich, HPLC grade) and analyzed by HPLC using an Alliance Waters 2690 separation module and a Jordi Gel DVB polyamine column (250 mm × 4.6 mm, Alltech) at 40 °C. The gradient program started from 100% heptane to 100% CH_2Cl_2 in 15 min and then to 80/20 CH_2Cl_2/THF in 25 min. After 5 min, the eluent was changed to 100% CH_2Cl_2 in 5 min, after which the gradient was changed to 100% heptane in 5 min. Detection was carried out using a multiwavelength and multiangle PL-EMD 960 evaporative light scattering detector (ELSD) (Polymer Laboratories), and data acquisition was done using Millennium-32 3.05 software.

Data Analysis. When using the ELSD detector to analyze the samples from the exchange reactions, two fundamental problems arise. First, the detector response signal is not the same for the macroinitiator (R−Br) and for the hydroxy-functional species (R−OH), which also elute at different eluent composition. Second, the detector response signal is not simply linearly dependent on concentration but is scaled with a power law.[24] These problems can be solved by calibrating the ELSD detector for all compounds that are important in eq 2. The hydroxy-functional species, however, were not available as pure compounds, and therefore, direct calibration for these compounds was not possible. Fortunately, [R−Br] + [R−OH] = constant in each experiment. This mass balance holds when R• is exclusively trapped by the nitroxide and transformed into R−OH. When neglecting transfer reactions, the probability of R• being trapped by hydroxy-TEMPO follows eq 3.

$$p_{\mathrm{trapping}} = \frac{k_{\mathrm{trap}}[\mathrm{T}]}{k_{\mathrm{trap}}[\mathrm{T}] + k_{\mathrm{deact}}[\mathrm{Cu(II)}] + k_t[\mathrm{R^\bullet}]} \qquad (3)$$

When using the concentrations in the exchange experiments, and appropriate values for the trapping rate constant ($k_{\mathrm{trap}} \approx 10^8$ L mol^{-1} s^{-1} [25]), the termination rate constant ($k_t \approx 10^8$ L mol^{-1} s^{-1} [26]), and deactivation rate parameter ($k_{\mathrm{deact}} \approx 10^7$ L mol^{-1} s^{-1} [19]), and deactivator concentration ([Cu(II)Br] $\approx 10^{-3}$ M), all radicals are clearly trapped by the nitroxide. Using the

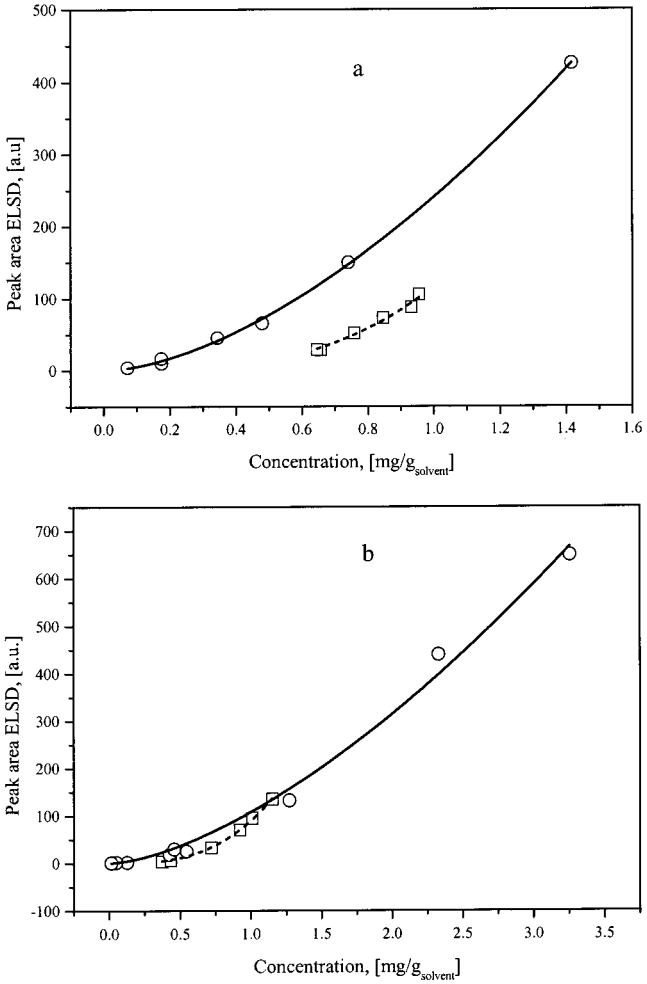


Figure 1. Calibration curves for ELSD quantification in HPLC analyses: (a) PS−Br dormant species (—) and PS−OH trapped species (- - -). (b) PBA−Br dormant species (—) and PBA−OH trapped species (- - -).

mass balance, we can construct a calibration curve for R−OH from the calibration curve for R−Br. In general, the data were analyzed by first correcting the ELSD chromatograms with the calibration curves for the nonlinear concentration dependence. Then, using the mass balance, the chromatograms were normalized on the total peak area. The relative peak area of the R−Br species was then calculated and used in **(2)**.

Results and Discussion

The calibration curves for the detector response signal as a function of concentration for PS−Br and PS−OH and PBA−Br and PBA−OH are depicted in Figure 1, a and b, respectively. The calibration curves for PS−Br and PBA−Br measured with calibration samples with known concentrations are very well described by a power law, as are the calibration curves for PS−OH and PBA−OH. These calibration curves will therefore be used in further quantitative analysis of the exchange reactions. An example of a series of HPLC chromatograms for an exchange reaction in xylene using PS−Br is shown in Figure 2. The dormant species and the hydroxy-functional species are well separated, thus allowing reliable quantitative data analysis. Figure 3a,b shows the pseudo-first-order plots according to **(2)** for PS−Br and PBA−Br in xylene.

When extracting data from the pseudo-first-order plots, one should always look closely at the HPLC chromatograms to evaluate the accuracy of the data. This is especially important when almost all macroinitiator has depleted and the R−Br peak is very small compared to the R−OH peak. This is reflected in Figure 3, where the data points at large times deviate from pseudo-first-order behavior.

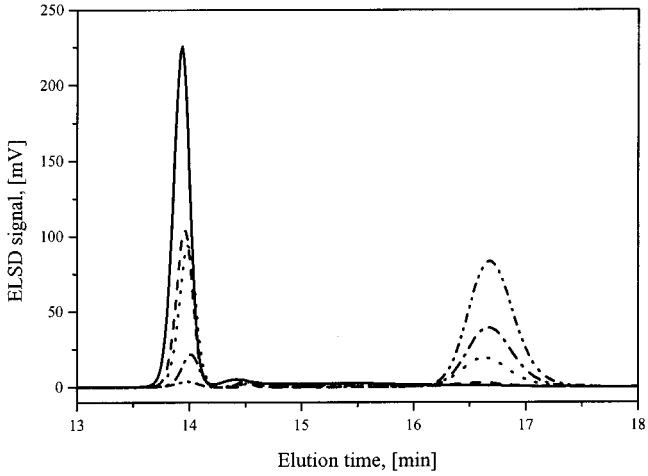


Figure 2. HPLC chromatograms for an exchange reaction with PS−Br in xylene at 110 °C at $t = 0$ s (—), $t = 60$ s (- - -), $t = 180$ s (···), $t = 300$ s (- · -), and $t = 600$ s (· - ·).

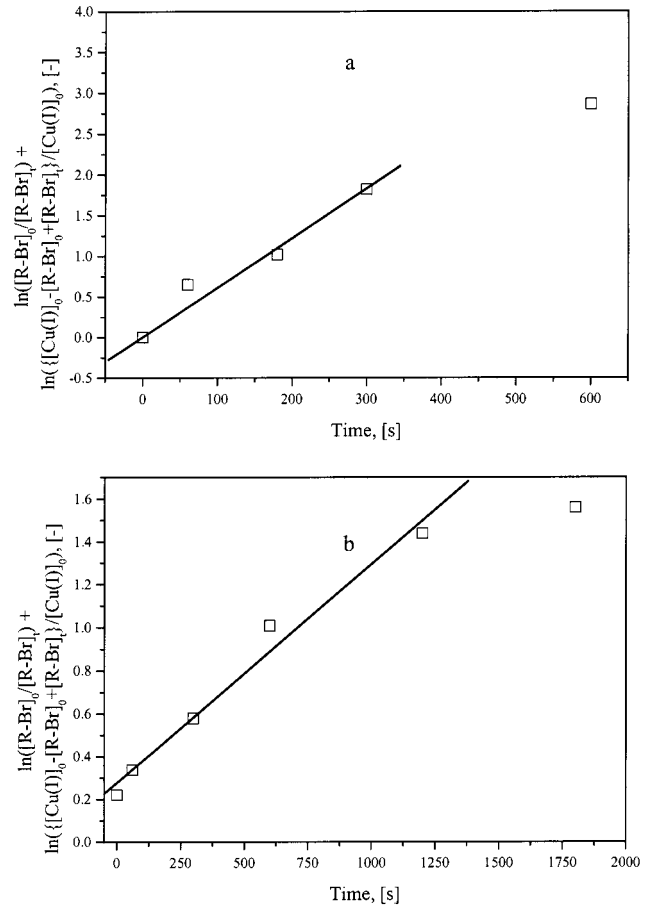


Figure 3. Pseudo-first-order plots of exchange reactions of PS−Br (a) and PBA−Br (b) in xylene at 110 °C.

The resulting activation rate parameters are 0.43 L mol^{-1} s^{-1} for PS−Br and 0.071 L mol $^{-1}$ s^{-1} for PBA−Br in xylene at 110 °C. The value for the activation rate parameter for PS−Br, k^S_{act}, is in very good agreement with data reported by Fukuda et al.,[19] who found a value of 0.45 L mol^{-1} s^{-1}. The value for the activation rate

Table 1. Activation Rate Parameters for PS−Br and PBA−Br at 110 °C in Various Solvents[a]

solvent	dielectric constant[a]	k_{act} (L mol^{-1} s^{-1}) PS−Br	k_{act} (L mol^{-1} s^{-1}) PBA−Br
xylene	2.14	0.43	0.071
dioxane	2.06	0.17	0.033
BuAc	4.04	0.27	0.086
1-butanol	8.88	0.48	4.3
DMF	27.3	0.26	0.088

[a] Detailed experimental conditions are listed in the Experimental Section. [a] Lide, D. R.; Frederikse, H. P. R. *CRC Handbook of Chemistry and Physics*, 78th ed.; CRC Press: New York, 1997.

parameter for PBA−Br, k^{BA}_{act}, is almost a factor 6 lower than k^{S}_{act}. This is probably due to the lower stability of the PBA radical. The results for the exchange reactions in dioxane, butyl acetate, 1-butanol, and DMF are listed in Table 1. The data in Table 1 demonstrate that the solvent influences the activation rate parameters. Dioxane seems to impede dissociation of both dormant species, although it has a dielectric constant similar to that of xylene. The decrease in activation rate parameters may be due to interactions between dioxane and the copper complex, since ethers may act as ligands.[22] Coordinating solvents may saturate the coordination sphere of the copper complex temporarily and decrease the reaction rate.

The influence of butyl acetate on the activation rate parameters of PS−Br and PBA−Br is inconsistent and does not support Matyjaszewski's[18] proposal that activation of the PS macroinitiator is enhanced in more polar media. On the contrary, the activation of a PS macroinitiator is hampered in butyl acetate, resulting in lower k^{S}_{act}. We do not have an explanation for this observation. The increase in k^{BA}_{act} is very small and can be explained by stabilization of the radical by butyl acetate. The radical is more easily formed, which increases k^{BA}_{act}. To further investigate the effect of polar media, we also performed exchange experiments in 1-butanol. The activation rate parameter for PBA macroinitiator dramatically increases from 0.071 L mol^{-1} s^{-1} in xylene to 4.3 L mol^{-1} s^{-1} in 1-butanol. Although this is consistent with increasing k^{BA}_{act} with increasing solvent polarity, the effect is peculiarly pronounced and may be related to the hydroxy-functional group in the solvent. Similarly, phenols and water dramatically increase the polymerization rate of MMA.[27,28] However, the hydroxy group of the hydroxy-TEMPO does not affect the activation rate parameter in xylene compared to literature values, although it is present in a relatively high concentration in the exchange reactions. We are currently investigating the origin of these effects. The overall effect of 1-butanol on k^{S}_{act} is limited, since the negative effect of polarity is, presumably, compensated by the enhancing effect of the presence of the hydroxy group. DMF combines a high polarity with the ability to act as ligand in the copper complex, which should decrease k^{S}_{act}. This is indeed the case, although the effect is not as pronounced as we might expect. For k^{BA}_{act}, polar solvents clearly enhance activation, although the ability to act as a ligand depresses the activation. The value of 0.088 L mol^{-1} s^{-1} suggests that solvent polarity dominates.

In all of the data analyses, the presence of any dead material in the macroinitiators is neglected. Although this is not correct, the HPLC peak for the dormant species, R−Br, almost completely disappears at the end of the reaction (e.g., Figure 2), which indicates that the amount of inactive chains in the macroinitiator is negligible (<2%).

Table 2. Effects of Solvent Polarity, Coordinating Ability, and Presence of Hydroxy Groups on Activation Rate Parameters

solvent	PS−Br	PBA−Br
polarity	−	+
coordinating ability	−	−
hydroxy group	+	+

Conclusions

The activation rate parameters for PS and PBA macroinitiators in ATRP (k^{S}_{act} and k^{BA}_{act}, respectively) have been determined using a combination of exchange reactions with hydroxy-TEMPO with subsequent analysis by HPLC. This method does not involve monomer and can be applied using a wide variety of solvents. The validity of the method has been assessed by comparing the results with those available in the literature, and they are in good agreement. A number of solvents, varying in polarity, coordinating ability, and presence of hydroxy groups, have been used to evaluate their effect on the activation rate parameters of PS and PBA macroinitiators in ATRP. Increasing solvent polarity decreases the activation rate parameter of a PS macroinitiator and increases the activation process of a PBA macroinitiator. The ability to act as ligand in the copper complex decreases the activation rate parameters for both macroinitiators: in dioxane k^{S}_{act} = 0.17 L mol^{-1} s^{-1} (compared to 0.43 L mol^{-1} s^{-1} in xylene) and k^{BA}_{act} = 0.033 L mol^{-1} s^{-1} (compared to 0.071 L mol^{-1} s^{-1} in xylene). Finally, the presence of hydroxy groups seems to increase both k^{S}_{act} and k^{BA}_{act}, although we have no explanation for this observation. The effects of solvent polarity, coordinating ability, and the presence of hydroxy groups are summarized in Table 2.

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