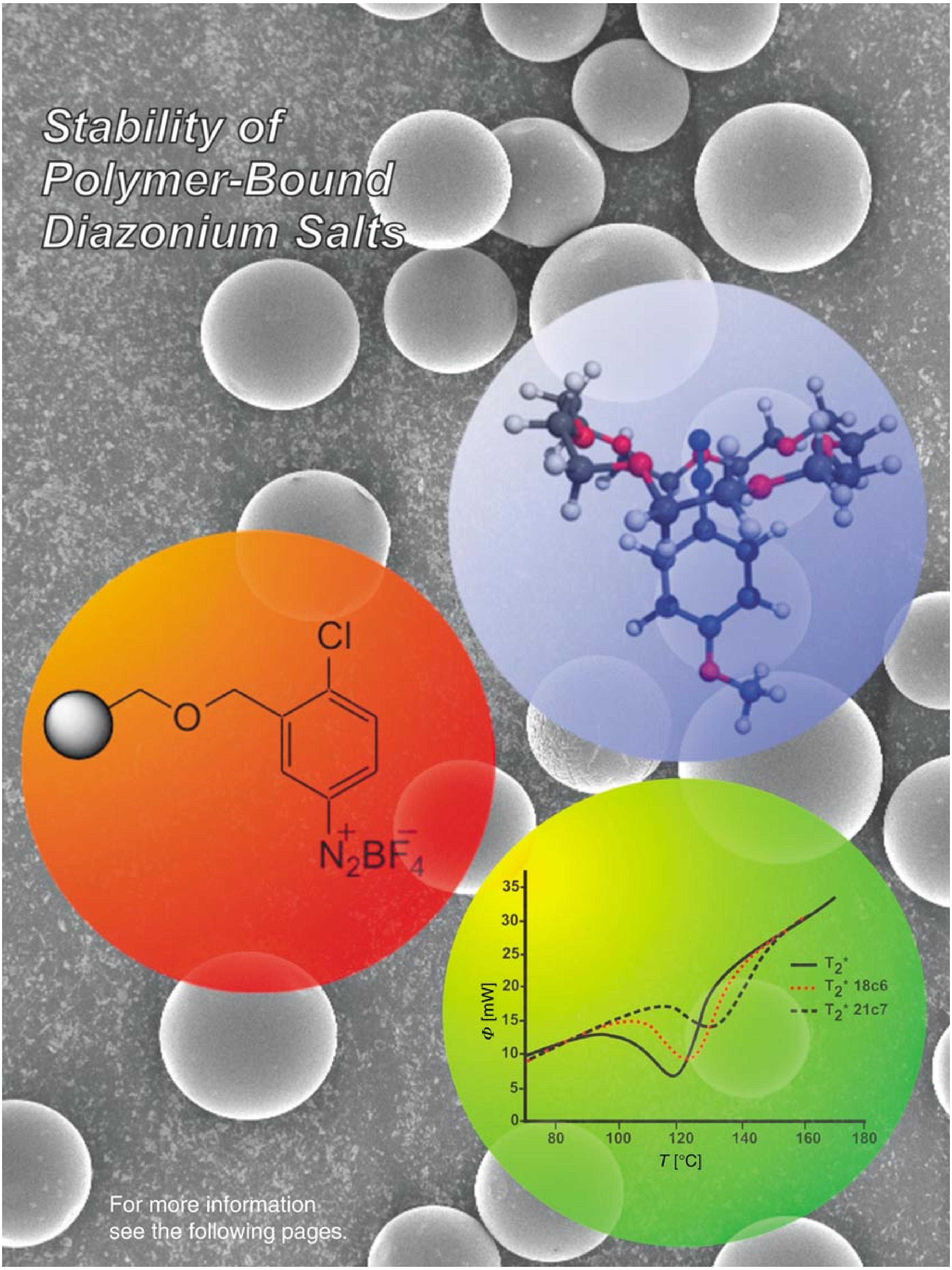

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The Structural Influence in the Stability of Polymer-Bound Diazonium Salts

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Abstract: Various new diazonium ions on a polymeric support that have a variety of counterions and complexation with crown ethers have been prepared, and the thermal stability of these resins over a larger temperature interval has been investigated. Nonisothermal kinetics applied to DSC data have been used predicting the lifetime of the resins.

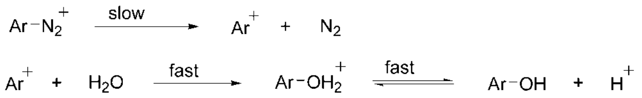
Keywords: azo compounds • differential scanning calorimetry • kinetics • resins • solid supports

Introduction

Stability of diazonium ions: Diazonium ions represent one of the most versatile functional groups in organic chemistry.[1,2] The most important reactions of aromatic diazonium ions are Sandmeyer, Schiemann, Meerwein, Pschorr, and Gomberg–Bachmann reactions, but also the Heck reaction[3] and the formation of triazenes[4] and azo compounds[5] represent important processes. Diazonium ions are also of interest in theoretical chemistry. In more recent theoretical works they are considered as electron-donor/acceptor complexes between a phenyl cation and a nitrogen molecule.[6,7]

The property that limits the application of diazonium ions most is their lability. Aromatic diazonium ions undergo fragmentation to nitrogen and reactive phenyl intermediates.

The decomposition of diazonium salts was investigated in 1940 by Crossley,[8] who showed that the rate of nucleophilic substitution of the diazonio group is independent from the concentration of the nucleophiles and is proportional to the rate of hydrolysis. This reaction proceeds by an S_N1 mechanism, for which the rate-determining step is the irreversible dissociation of the diazonium ion into an aryl cation and nitrogen, followed by a fast reaction of the cation with nucleophiles in the reaction mixture (Scheme 1).



Scheme 1. S_N1-like decomposition of diazonium ions.

Ionic[9] and radical[10] pathways, initiated by single-electron transfer reactions, are also known.

In general, an S_N1 type mechanism is considered, although there are indications for an S_NAr type mechanism in the presence of nucleophiles. In 1952 Lewis[11] and Hinds found that the decomposition of 4-nitrobenzenediazonium ion in water is proportional to the concentration of the added nucleophile. Although various other examples favor an S_N2 mechanism, the effect of substitution as determined by Crossley and later reconfirmed by Schulte-Frohlinde and Blume[12] cannot explain this mechanism. Instead of an increase of decay caused by substituents (e.g., 4-NO_2), as required for such a mechanism, nearly all substituents in *meta*- or *para*-position led to a higher stability. These substitution effects can be large, a factor of 10^5 can be found between the fastest and the slowest decomposition of monosubstituted diazonium salts.

The activation energy for the dediazotation of the benzenediazonium ion and substituted derivative was determined by Crossley[11] in water ($E_a = 114\,\mathrm{kJ\,mol^{-1}}$ for $C_6H_5N_2^+$); later other groups determined it for various other solvents. The activation enthalpy is quite high ($\Delta H^{+} = 108\,\mathrm{kJ\,mol^{-1}}$ for $C_6H_5N_2^+$) and is within the same range in for most of the nucleophilic aliphatic substitution reactions that follow an S_N1-type mechanism. In contrast, the corresponding activation entropies have a high positive value ($\Delta S^{+} = 33\,\mathrm{J\,K^{-1}\,mol^{-1}}$), compensating partly the high value of ΔH^{+}.

The kinetics of dediazotation of 3- and 4-substituted arenediazonium ions cannot be explained by a Hammett equation, but with a DSP (dual substituent parameter) equation

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as demonstrated by Dickinson and Eaborn[13] in 1959. This equation takes the mesomeric and inductive effects of the substituents independently into account and leads to a nearly perfect correction of calculated and experimentally verified rate constants[1] (See Figure 1).

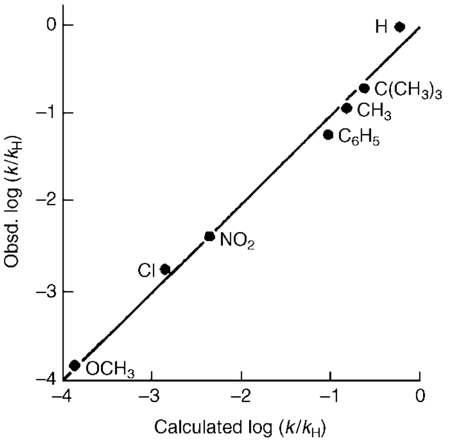


Figure 1. DSP-Plot of *para*-substituted benzenediazonium ions in 0.1 M HCl at 25 °C.[14] The equation $\log(k_x/k_H) = \sigma_F\rho_F + \sigma_R^+\rho_R$ was used.[1]

The DSP plot explains effects of substitution on the basis of an S_N1 reaction; however, it does not explain the bimolecular reaction type, which is frequently observed for such systems.

Glaser et al. developed a method that explains the change of stability of two fragments X and Y, which result from the decomposition of X–Y.[15] The enthalpy of dediazotation of a diazonium ion would result as a sum of two components: the energy difference ΔE_1 between the diazonio group in the diazonium ion and a free nitrogen molecule (N_2), and the energy difference ΔE_2 between the phenyl cation and the C_6H_5 fragment of the diazonium ion. The energy values ΔE_1 and ΔE_2 are called fragment-transfer energies. The sum of ΔE_1 and ΔE_2 is the bond dissociation energy ΔE_{diss}. Stabilization of the bond results in a positive dissociation energy.

For the benzenediazonium ion, the following values were obtained: $\Delta E_1 = -59.0\ \mathrm{kJ\,mol^{-1}}$, $\Delta E_2 = 164.9\ \mathrm{kJ\,mol^{-1}}$, and $\Delta E_{diss} = 105.9\ \mathrm{kJ\,mol^{-1}}$. This means, that throughout the decay the fragment N_2 is stabilized and the fragment C_6H_5 is destabilized. This is in agreement with chemical intuition and the experiment. The bond stabilization of both fragments is therefore not because of their association; it is a result of a destabilization of the phenyl cation rather than the stabilization of the N_2. The bond dissociation energy is close to the experimental activation energy in solution ($E_a = 114\ \mathrm{kJ\,mol^{-1}}$ for $C_6H_5N_2^+$[26]). When taking the electron correlation and vibrational zero-point energy into account, the value one obtains is even closer: $E_a = 115\ \mathrm{kJ\,mol^{-1}}$.

Results and Discussion

Stabilization of diazonium ions by crown ethers: Besides the change to larger non-nucleophilic counterions,[16] another possibility for the stabilization of diazonium ions is the complexation with suitable crown ethers. The first diazonium salt crown ether adduct was isolated in 1975 by Haymore and identified as a 1:1 complex.[1,17] The ORTEP structure of this benzenediazonium hexafluorophosphate complex with [18]crown-6 is accessible.[18] The structures of 4-methoxybenzenediazonium tetrafluoroborate with [21]crown-7[19] (Figure 2) or dibenzo[24]crown-8, respectively, have also been published.[20] All these structures show that the crown ether complexes the diazenyl group.

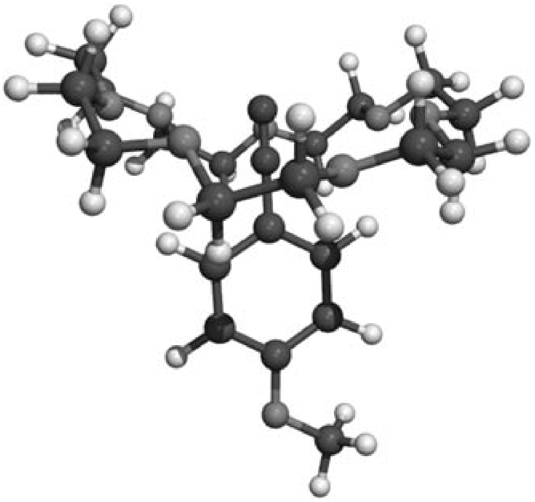
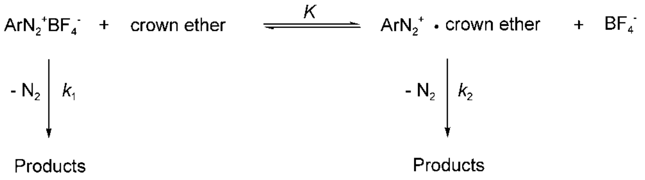


Figure 2. Structure of the complex of 4-methoxybenzenediazonium tetrafluoroborate with [21]crown-7; the counterion tetrafluoroborate was omitted for clarity. Taken from data of reference [19]

However, there is a significant difference for the crown ether sizes. While [18]crown-6 is the smallest crown ether suitable for complexation of diazonium ions, [21]crown-7 is the strongest complexing and stabilizing agent for benzenediazonium ion.[21] Scheme 2 demonstrates the kinetics of the complex diazonium ion decay. The complexation equilibrium constant (K) characterizes the stability of these complexes. The thermal decay of the uncomplexed (k_1) and the complexed (k_2) ions reflects their respective stabilities.



Scheme 2. Decay and reaction rates of the dediazotation of substituted arene diazonium tetrafluoroborates (k_1 and k_2) and complex equilibrium constant (K) with crown ether.

The Table 1 shows the values for the complex equilibrium constant and the decay rates for different substituted arenediazonium ions. The stability clearly depends on the substitution pattern; this results in the increase in stabilization by three orders of magnitude by complexation. It has been shown that a linear Hammett relationship ($\rho = 0.65$) was

Table 1. Rate of dediazotation of substituted arenediazonium tetrafluoroborates (k_1 and k_2) and complex equilibrium constant (K) with [18]crown-6 (18C6), [21]crown-7 (21C7) and dicyclohexyl-24-crown-8 (DCH24C8) in 1,2-dichloroethane at 50 °C.[22]

Substituent	Crown ether	K 10^4 L mol^{-1}]	k_1 [10^{-3} s^{-1}]	k_2 [10^{-5} s^{-1}]
p-CH$_3$	18C6	2.47	0.144	0.22
	21C7	30.8		0.032
	DCH24C8	1.80		1.4
m-CH$_3$	18C6	3.36	5.68	6.2
	21C7	36.0		3.0
	DCH24C8	1.48		16
H	18C6	4.69	1.13	1.8
	21C7	50.6		0.16
	DCH24C8	2.76		6.3
m-CH$_3$O	18C6	6.03	8.23	10
	21C7	70.2		0.63
	DCH24C8	3.53		19
p-Cl	18C6	7.72	0.00235	0.023
	21C7	15.4		0.004
	DCH24C8	2.05		0.039
m-COCH$_3$	18C6	10.4	2.01	1.4

found between log K and σ^{++} values associated with the *para* substituent.[23]

The rate of dediazotation for the complexes with [21]crown-7 is the slowest and the complex equilibrium constant K is the highest. The absolute value of the decay rate of the free ions as well as the complex with crown ether is at minimum with p-Cl-$C_6H_4N_2BF_4$. This means that, in this evaluation, the diazonium ion p-Cl-$C_6H_4N_2BF_4$ is the most stable both in the free form and in the complexed state. According to the results in Table 1, p-Cl-$C_6H_4N_2BF_4$ in the uncomplexed form is approximately 3500 times more stable than m-CH_3O-$C_6H_4N_2BF_4$, which indicates that the T2 linker[24,25] is the most unstable diazonium salt. Furthermore, p-Cl-$C_6H_4N_2BF_4$ is stabilized with [18]crown-6 by a factor of 10 and with [21]crown-7 by a factor of 60. The calculated half-life time ($t_{1/2}$) of the decay (for first-order kinetics) under the given conditions (50 °C in 1,2-dichloroethane) is listed in Table 2.

Table 2. Estimation of half-life time of the dediazotation (taken from data in Table 1).[a]

Diazonium ion	$t_{1/2}$ (50 °C) [s]	$t_{1/2}$ (20 °C) [s]
m-CH_3O-$C_6H_4N_2BF_4$	84	3798
p-Cl-$C_6H_4N_2BF_4$	0.3×10^6 (≈3.5 days)	13.3×10^6 (≈154 days)
p-Cl-$C_6H_4N_2BF_4$·[21]crown-7	17×10^6 (≈200 days)	781×10^6 (≈9040 days)

[a] The half-life time was calculated according to $t_{1/2} = \ln 2/k$. The value for $t_{1/2}$ (20 °C) was calculated via the Arrhenius equation ($k = Ae^{-E_A/RT}$) from the value for $t_{1/2}$ (50 °C). An activation energy of $E_A = 100$ kJ mol^{-1} was assumed.

The complexation with crown ethers can be followed by IR spectroscopic methods. The IR spectra show that the N≡N-vibration upon complexation with [18]crown-6 is shifted to higher wavenumbers. Therefore, the four complexes in Table 3 show a shift by of 20–29 cm^{-1}. In contrast, the $\nu_{N\equiv N}$ values of the [21]crown-7 complexes are, with the exception of p-CH_3O, in within the region of ±5 cm^{-1} for the uncomplexed ions.

Table 3. IR spectra of arenediazonium tetrafluoroborates (p-$XC_6H_4N_2BF_4$) and of their crown ethers in Nujol[26]

Substituent	$\tilde{\nu}_{N\equiv N}$[cm^{-1}] Uncomplexed	Complex with [18]crown-6	Complex with [21]crown-7
H	2300	2320	2300
p-tBu	2277	2306	2282
p-CH$_3$	2286	2315	2283
p-Cl	2297	2319	2302
p-CH$_3$O	2247		2261

To investigate the influence of a polymeric backbone, diazonium salts were immobilized on solid supports.

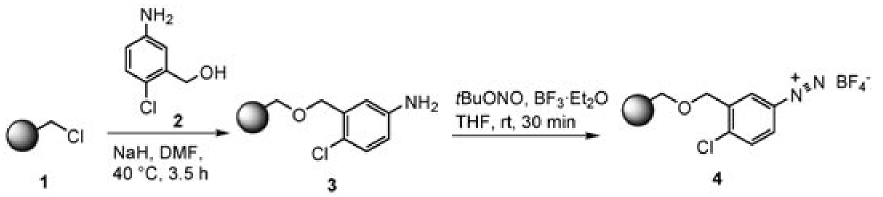
Diazonium ions on solid supports: Diazonium ions have been synthesized previously on cellulose[27,28] and macroporous supports,[29] and have been used for the immobilization of enzymes.[28] Benìs et al. showed,[30] that (p-aminophenylsulfonyl)ethyl-modified cellulose could be diazotized to give, according to the authors, a not very stable diazonium salt that could be coupled with β-naphthol to give the corresponding azo dye. Lipophilic supports are have been used in a sequence consisting of diazotation and subsequent reduction for the synthesis of hydrazines.[31] The diazotation of aliphatic amines in the presence of halide ions is a convenient method and has been used for the synthesis of Merrifield-type resins on a Multipin-support™.[32]

We have synthesized diazonium ions with different substitution pattern and used them for the synthesis of triazenes.[33–36] Rademann et al. used the T2-*para* resin for the synthesis of triazenes,[37] while Struber et al. developed solid-phase bound triazenes, based on nitration and further functionalization of polystyrene, and investigated their chemical and thermophysical properties.[38]

There is, however, less knowledge on the stability of diazonium ions on solid supports. In particular, the influence of the substitution pattern is of interest.

Synthesis of immobilized diazonium ions: Our linker for secondary amines (T2),[8] with an m-methoxy-type substitution, was only synthesized as an intermediate and had to be stored and handled below 0 °C to avoid decomposition. Our aim was to develop a temperature-stable diazonium ion on a solid support, that is, to combine the broad chemical usage of the diazo chemistry and the simple handling of solid-phase organic chemistry. Therefore, various immobilized diazonium resins were prepared. Particularly, based on the theoretical considerations by Glaser,[39] as well as on experimental results[14] showing that *para*-chloro- and methoxy-substituted diazonium ions are highly stable, the chlorine-stabilized immobilized diazonium ion T2*[40] and the so-called T2-*para* resin were prepared.

The resins were prepared according standard methods by using the Merrifield resin (chloromethylated polystryrene, cross-linked with 1–2 % divinylbenzene, 100 mesh, ca. 1 mmol g^{-1}) as a solid support. For the T2* linker, the required aminobenzylalcohol **2** was synthesized in two steps from commercially available 2-chloro-5-aminobenzoic acid. The esterification was carried out by using trimethyl chlorosilane in methanol, which gave rise to the methyl ester. The ester was reduced then with lithium aluminum hydride ($LiAlH_4$) in THF to the corresponding benzyl alcohol **2**. Coupling to Merrifield resin proceeds with *O*-selectivity if carried out with sodium hydride (Scheme 3).



Scheme 3. Syntheses of the immobilized diazonium ion **4**.

A series of new polymer-bound resins (**4**–**10**) were designed taking the influence of substituents into account. Only resin **5** contained the diazonium group in the *ortho* position, which might not only lead to side product such as cyclization, but would also have a detrimental effect on the possible coordination of crown ethers.[23] The resins used for polymer-bound diazonium ions **5**–**10** were prepared by coupling either the phenolate, alcoholate, or carboxylate onto Merrifield resin. The loadings of the resins were determined by CHN analysis.

The subsequent diazotation reaction of the amino resins with *tert*-butyl nitrite (*t*BuONO) and bortrifluoride etherate ($BF_3{\cdot}Et_2O$) in THF between 0 and −10 °C led to the polymer-bound diazonium ions **4**–**10**. The chloride resin **11** was obtained by starting from the corresponding ammonium chloride resin.

It is interesting to note that the resin **8** immediately turned dark after preparation, an indication that the mesomeric diazocyclohexadieneoxyl structure might bring an important contribution for stabilization.[41] In addition, the phenol formed upon dediazotation might also lead to crosslinking. If the diazotation is performed at room temperature or 0 °C, different resins are obtained with distinct thermochemical features (see below).

The exchange of the counterion tetrafluoroborate was accomplished by using the resin **10** to give the hexafluorophosphate resin **12** after treatment with potassium hexafluorophosphate.

Complexation with crown ethers: The stability of diazonium ions can be increased by complexation with crown ethers,[25] with [21]crown-7 showing the highest thermal stability. Therefore the polymer-bound diazonium ion **4** was shaken with [18]crown-6 or [21]crown-7 to give the new resins **4·18c6**, and **4·21c7**, respectively (Figure 3).

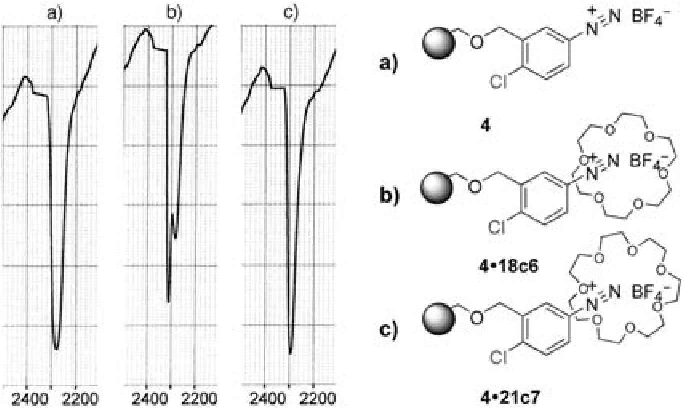
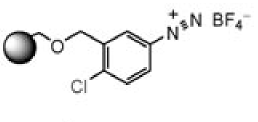


Figure 3. Part of IR spectra of polymer-bound diazonium ions; $\nu(N{\equiv}N)$ of the diazonium functionality being shown, that is a) uncomplexed, b) partly complexed as [18]crown-6 complex or c) as [21]crown-7 complex.

Spectroscopic properties of the immobilized diazonium ions: All resins prepared (**4·18c6**, **4·21c7**) were examined by IR spectroscopy. The complexation with [18]crown-6 shifts the N≡N stretching vibration clearly to higher wave numbers (shifts of 20–29 cm^{-1} are mentioned in literature[25]), whereas the complexation with [21]crown-7 leads to small shifts only (about +5 cm^{-1} relative to the uncomplexed diazonium ion). In spite of a high excess of crown ether the polymer-bound diazonium salt **4** could not be transformed into its [18]crown-6 complex **4·18c6** quantitatively, because the rates of complexation are lower than in the case of the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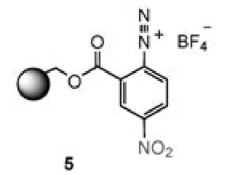
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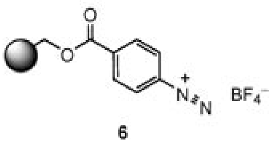
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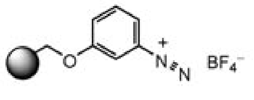
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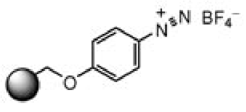
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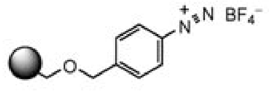
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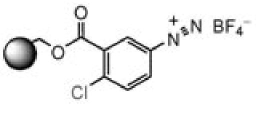
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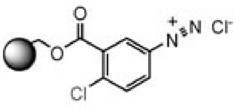
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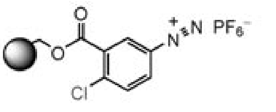
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corresponding [21]crown-7 complexes. Therefore, it is possible that the [18]crown-6 ether is partly washed off during workup.

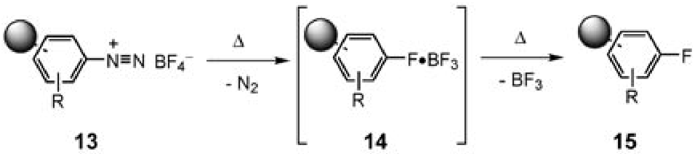
The stability of immobilized diazonium salts

Elemental analysis: The stabilities of the diazonium ions were investigated by thermal decomposition. Isothermal decomposition studies were performed to give an experimental value for the decay of nitrogen during normal laboratory use. The studies where carried out at 60 °C, and the conversion was examined by CHN combustion analysis.[42] Resin samples were kept isothermally at 60 °C and after 1, 6, 9, 34, and 48 h samples were taken and cooled, and the nitrogen content examined. The experimentally determined half-life time of resin **4** is eleven hours at 60 °C. Analogously the resins **4·18c6** and **4·21c7** were examined. It is quite puzzling that, although thermochemically more stable than the uncomplexed resin **4**, the resin **4·18c6** is less kinetically stable. We explain this fact that the crown ether, which is not perfectly suitable, might facilitate the reduction to the parent hydrocarbon. The reduction of diazonium salts using alicyclic and cyclic ethers is known.[1]

Thermal analysis: The thermal stability of the resins **4**–**6**, **8**–**12**, **4·18c6**, and **4·21c7** has been investigated by the aid of DSC (differential scanning calorimetry). The resin **6** was also submitted to TGA (thermogravimetrical analysis) measurements.[43,44]

The TGA investigations of the resin **6** revealed that the full decomposition proceeds through a two-step process. The stoichiometric liberation of dinitrogen, recorded by TGA, is accompanied by an exothermic effect at around 140 °C observed on the DSC curve. Boron trifluoride apparently is still bound somehow to the resin and is liberated from the resin above 200 °C.

We may consider that for all resins, when heated, the compound releases first a nitrogen molecule resulting in heterolytic cleavage and a subsequent Schiemann-type reaction[45] (Scheme 4).



Scheme 4. Decomposition of diazonium ions **13**.

All resins exhibit a first exothermal decomposition between 90 and 180 °C (Table 4), with the exception of resin **7**, which is much less thermostable.

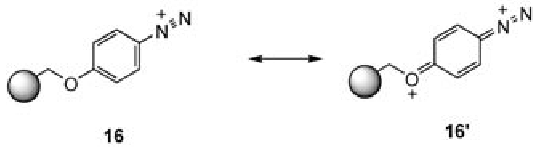
Table 4. Decomposition temperatures (T_{decomp}) for the resins **4**–**12** as determined from their DSC plots (heating rate 10 K min^{-1}).

Resin	T_{decomp}	Resin	T_{decomp}
4	114	**8**[a]	156
4·18C6	122	**8**[b]	147
4·21C7	130	**9**	93
5	147	**10**	134
6	105	**11**	87
7	–[c]	**12**	128

[a] Preparation of the resin at 0 °C. [b] Preparation of the resin at room temperature. [c] Rapid decomposition.

The DSC data show a reaction enthalpy of $\Delta_R H = -120$ kJ mol^{-1} for the fragmentation reaction, which is independent of complexation. The decomposition reaction follows a first-order kinetic, which is expected from both Scheme 4 and comparision to literature.[13] This reconfirms an S_N1-type mechanism of decomposition. The S_NAr-type mechanism would require the presence of a nucleophile. This is not likely since the resins have been washed and dried before usage.

The structural change of the diazonium ions results in changes of stability. The resin **7** was quite unstable and decomposes prematurely preventing the thermal analysis. The change to a *para*-alkoxy group dramatically increases the stability (resin **8**). However, depending on the diazotation method (see Experimental Section), apparently two different structures can be obtained. A possible, yet to be confirmed, hypothesis would be that the two resins inhibit different location of the counterion. Since the mobility of the counterion is limited because of being on a solid support without a solvent, it is possible that the two tautomeric structures (Scheme 5) are differently favored with different location of the counterion. However, the IR stretching ought to be the same. Alternatively, the alkoxybenzenediazonium–diazocyclohexadienyloxy mesomerism plays a major role for the stabilization of diazoniumphenolate. Further investigation might explain this finding.



Scheme 5. The alkoxybenzenediazonium–diazocyclohexadienyloxy mesomerism.

A carboxy group leads to greater stabilization than an alkoxymethyl group (**6** vs **9**). Comparing the resins **6**/**9** with **4**/**10**, we notice that the substitution of an alkoxymethyl group against a carboxy group is more efficient when placed in the *meta* position.

The resin **5** combines the stabilizing effects of the nitro group and the carboxy moiety, and together with the resin **8** is one of the most stable resins. All the above-mentioned effects are in good agreement with the DSP plot and Table 1.

The counterion increases the stability of the resin in the order chloride ≪ hexafluorophosphate ≈ tetrafluoroborate.

The influence of the complexation is quite remarkable, although in the range of the above-mentioned values. While the complexation with [18]crown-6 shifts the peak temperature to 122 °C, complexation with [21]crown-7 results in another increase, as already noticed in conventional diazonium salts.

The T2* resin **4** is, from a practical standpoint, the most useful, because the ether functionality is by far more stable than the hydrolytically sensitive ester group. The T2-*para* resin **8**, although thermally quite stable, is less attractive, due to its strong coloration and the formation of byproducts.

Thermochemical evaluation and half-life time predictions: The values for the activation energy (E_a), the pre-exponential factor (A) and the function of conversion degree α from Equation (1) have been calculated by different methods from the thermodynamical data obtained by DSC measurements (see Table 5). For more details of the mathematical calculations of these methods, see the Experimental Section.

$$\frac{d\alpha}{dt} = f(1-\alpha)\,A\exp\left(-\frac{E}{RT}\right) \tag{1}$$

Table 5. The values of the kinetic parameters E and A, calculated by various methods, for resin **4**.[46] Investigations on the thermal stability of a diazonium ion on solid support.

Methods	E [kJ mol^{-1}]	ln$A$ [min^{-1}]	$f(1-\alpha)$
iso-conversional methods		30.24 ± 1.2	$1-\alpha$
differential	100.0 ± 6		
integral	104.4 ± 5.1		
Kissinger	101.4 ± 5.3	–	–
invariant kinetic parameters	95.7 ± 1.7	28.55 ± 0.68	$1-\alpha$
"isothermal" parameters [Eq. (15)]	104.4 ± 1.2	30.62 ± 2.1	$1-\alpha$

For resin **4** (example resin) an activation energy (E_a) between 95.7 and 104.4 kJ mol^{-1}, and ln(A) between 28.55 and 30.62 min^{-1} was determined for a reaction obeying a first-order decay. The half-life time was analytically determined by elemental analysis by of isothermal decomposition at 60 °C to be 11.5 h (see Figure 4). The agreement of the calculated values with those determined experimentally is quite good. We concluded from the example (resin **4**) that the nonisothermal kinetic analysis allows us to predict the stability of the diazonium ions accurately enough. The results obtained for all the resins, in terms of activation energy, pre-exponential factor and half life-time, are summed up in Table 6.

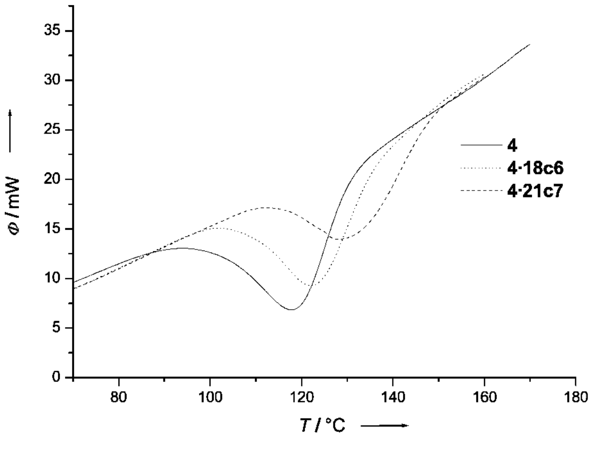


Figure 4. DSC measurements on solid-phase bound diazonium ions **4**, **4·18c6**, and **4·21c7**; the measurements were performed with 8–12 mg resin and heating rates of 10.0 °C min^{-1}.

The results in Table 6 show that the values calculated for the activation energy are all around of 113 kJ mol^{-1} (within ±13 %), very close to 114 kJ mol^{-1} obtained by Crossley through isothermal measurements.[3] On the other hand, the pre-exponential factor values range from 0.06 to 15530 × 10^{11} s^{-1}. These results support the idea that increasing the stability of the diazonium ion can be done at the expense of decreasing the entropy/decreasing the value of the pre-exponential factor.

Table 6. The values of the activation energies, pre-exponential factors, and half life times for the resins **4**–**12** as calculated by the described methodology.

Resin	E_A [kJ mol^{-1}]	A [× 10^{11} s^{-1}]	Half life-time at 20 °C Relative value vs resin **4**	 Days
4	105.6	25.53	1.00	21
5	129.9	1940	284.17	6100
6	112.9	742.8	0.69	15
8[a]	126.2	299	403.41	8700
8[b]	116.9	143.2	18.48	400
9	91.34	1.28	0.06	1.3
10	115.5	92.56	16.09	350
11	87.53	0.0641	0.24	5
12	130.9	15530	53.53	1150

[a] Preparation of the resin at 0 °C. [b] Preparation of the resin at room temperature. [c] Rapid decomposition.

The effect of the nature of the bond between the diazonium ion and the resin on the stability can be estimated by comparing the ester and ether bonds. Therefore we compared life-times at 20 °C for resins **4** and **10**, and **6** and **9**, respectively. In both cases the ratio is about 13 in favor of ester, suggesting an ester bond increases the stability more than the ether one does.

By comparing the resins **4** and **9**, and **10** with **6**, we noticed that the presence of chlorine in the *ortho* position leads to about 20 times higher stability of the resin. Also, by comparing the values of life-times at 20 °C for resins **10**, **11**, and **12** we observed that the increase of the volume of the counterion linked to diazonium ion leads to an increase of the stability, according to the rank: $Cl^- < BF_4^- \approx PF_6^-$.

The results of calculations, as well as of the isothermal test, show that the synthesized diazonium ions have a pretty good stability over a quite large interval of temperatures, and much above the values known for similar compounds.[2]

Conclusion

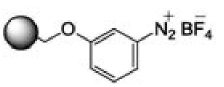
We synthesized and investigated the thermal stability of a diazonium ion bound to polymeric solid supports over a large range of temperatures from 0 to 200 °C by the help of DSC. In addition we used nonisothermal kinetic methods to infer the kinetic parameters. Two iso-conversional calculation methods (differential and integral) were applied and both led to close results. We also used Kissinger's method and the invariant kinetic parameters method and calculated the corresponding values of E, which were found to lie close to the range of values calculated by the iso-conversional methods. With the values of E obtained by the iso-conversional methods we calculated the kinetic function that fits best the experimental curve, and the resulting value of A. On the other hand, the values of the invariant kinetic parameters, E_i and A_i, were used for choosing the most suitable kinetic function out of a list of kinetic functions from the literature. In both cases the reaction order model, that is, first-order, was found to be most appropriate to describe the reaction both from fitting and from a physical point of view. An isothermal-like method was also used, giving similar values of the parameters and supporting the choice of the first-order model as the kinetic function. The values obtained for the kinetic triplet were finally shown to give a fairly good reproducibility of the initial DSC signal.

The resins **4**–**12** have good stability at room temperature and above with the exception of resin **7**, which decomposes at lower temperature. We can conclude that ester-bound diazonium-ions are more stable than ether-bound ones (**4**/**10** and **6**/**9**). Chlorine in *ortho* position to the linkage on the resin stabilises the diazonium resin. The size of the counterion plays an important role in the stability; bigger ones give more stability than smaller ones (**10**, **11**, **12**).

The calculated parameters E and A, and kinetic function, $f(1-\alpha)$, were further used for a half-life time prediction at various temperatures. The results of calculations were compared and suggestions on how to design a diazonium ion with high thermal stability were underlined.

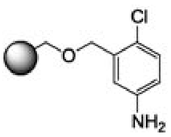
Experimental Section

All resins were characterized by IR spectroscopy, loading and conversions were valued by CHN combustion analysis. Experimentally examined loading of the resins can be correlated very well with the results from CHN-combustion analysis. Loadings of the used chloromethylpolystyrene were between 0.6 and 1.4 mmol g^{-1}. All new compounds were characterized completely or compared to known substances.

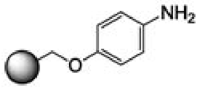


3-Diazoniophenyl-1-oxymethylpolystyrene tetrafluoroborate (**7**): A dry 500 mL, three-necked round-bottom flask was fitted with a mechanical stirrer, gas-inlet, and addition funnel. The apparatus was purged with argon and charged with dry DMF (250 mL) and sodium hydride (63.0 mmol, 1.51 g, 60 % in paraffin; 2.52 g in total). After addition of the Merrifield-resin (**1**; 20.0 g, 12.8 mmol, loading = 0.64 mmol g^{-1}), *m*-aminophenol (6.9 g, 63 mmol) was added portionwise (caution: H_2 evolution). After a reaction time of 20 h, the resin was purified by washing on an inert gas frit with solvents (three times with each; ca. 20 mL for each solvent per 1.00 g resin): THF, Et_2O, and MeOH. Subsequently the resin was dried in vacuum. IR (KBr): $\tilde{\nu}$ = 3390, 3200, 3080, 3060, 3020, 2910, 2840, 2640, 2600, 2310, 2340, 2380, 2260, 2110, 1940, 1870, 1800, 1710, 1670, 1620, 1590, 740, 690 cm^{-1}; elemental analysis calcd (%) for $C_{125}H_{125}ON$ (1655.0): C 90.63, H 7.55, N 0.85; found: C 89.90, H 8.03, N 0.89.

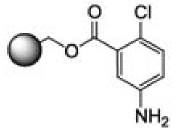
The amine resin (10.0 g, 6.4 mmol) was suspended in dry THF (150 mL) and cooled by means of a cold bath (EtOH/dry ice) to −20 °C. After 20 min, $BF_3\cdot Et_2O$ (6.9 mL, 7.7 g, 54 mmol) was added, followed after 5 min by *t*BuONO (5.7 mL, 5.0 g, 49 mmol). After a reaction time of 30 min, the mixture was collected in an inert gas frit, filtered, and washed with chilled THF (4 × 15 mL g^{-1} resin). The resin was washed on an inert gas frit with solvents (three times with each; ca. 20 mL for each solvent per 1.00 g resin): THF, Et_2O, and MeOH. Subsequently the resin was dried in vacuo.



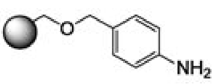
(5-Amino-2-chlorophenyl)methyl-1-oxymethylpolystyrene (3): A dry 500 mL, three-necked round-bottom flask was fitted with a mechanical stirrer, gas-inlet, and addition funnel. The apparatus was purged with argon and charged with dry DMF (100 mL) and sodium hydride (0.64 g, 26.8 mmol, 60 % in paraffin). After addition of Merrifield-resin (**1**; 5 g, 5 mmol, loading = 0.64 mmol g^{-1}), 5-amino-2-chlorbenzylalcohol (2.1 g, 13.4 mmol) was added portion wise (caution: H_2 evolution). After a reaction time of 4 h at 40–45 °C, it was quenched with saturated ammonium chloride solution (10 mL), and the resin was purified by washing on an inert gas frit with solvents (three times with each, ca. 20 mL for each solvent per 1.00 g resin): THF, Et_2O, and MeOH. Subsequently the resin was dried in vacuo. Elemental analysis calcd (%) for $C_{85}H_{86}NOCl$ (1172): C 87.03, H 7.34, N 1.19; found: C 86.38, H 8.20, N 0.77; loading: 64 %.



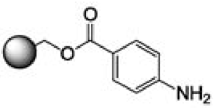
(4-Aminophenoxy)methylpolystyrene: The procedure described for the preparation of **3** was followed. The reaction starting from NaH (0.64 g, 26.8 mmol), Merrifield resin (5 g, 5 mmol) and 4-aminophenol (1.46 g, 13.4 mmol) in DMF (ca. 100 mL) at 40 °C for 4 h yielded the resin. Elemental analysis calcd (%) for $C_{84}H_{85}NO$ (1123): C 89.76, H 7.57, N 1.25; found: C 89.16, H 7.13, N 0.92; loading: 73 %.



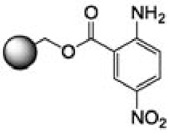
(5-Amino-2-chlorophenyl)carboxymethylpolystyrene: The procedure described for the preparation of **3** was followed. The reaction starting from NaH (0.64 g, 26.8 mmol), Merrifield resin (5 g, 5 mmol), and 5-amino-2-chlorbenzoic acid (2.29 g, 13.4 mmol) in DMF (ca. 100 mL) at 40 °C for 4 h yielded the colorless resin. Elemental analysis calcd (%) for $C_{85}H_{84}O_2NCl$ (1185.5): C 86.04, H 7.09, N 1.18; found: C 88.17, H 7.61, N 0. 84; loading: 71 %.



(4-Aminophenyl)methyl-1-oxymethylpolystyrene: The procedure described for the preparation of **3** was followed. The reaction starting from NaH (0.64 g, 26.8 mmol), Merrifield resin (5 g, 5 mmol), and 4-aminobenzylalcohol (1.65 g, 13.4 mmol) in DMF (ca. 100 mL) at 40–45 °C for 16 h yielded the colorless resin. IR (KBr): $\tilde{\nu}$ = 3464 (m, ν_{as}(N–H)), 3381 (m, ν_s(N–H)), 3081 (m), 3058 (m), 3023 (m, ν_{Ar}(C–H)), 2912 (s, $\nu(CH_2)$), 2850 (s, $\nu(CH_2)$), 1943 (m), 1872 (m), 1803 (m), 1678 (m, δ(N–H)), 1598 (s, ν_{Ar}(C=C)), 1444 (m, δ(C–H)), 1067 (s, ν(C–O)), 840 (m), 820 (m), 743 (s), 694 cm^{-1} (s). elemental analysis calcd (%) for $C_{85}H_{87}NO$ (1137): C 89.71, H 7.65, N 1.23; found: C 89.99, H 6.62, N 0.81; loading: 66 %.

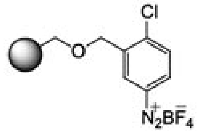


(4-Aminophenyl)carboxymethylpolystyrene: The procedure described for the preparation of **3** was followed. The reaction starting from Cs_2CO_3 (3.05 g, 9.36 mmol), Merrifield resin (5 g, 5 mmol), and anthranilic acid (2.05 g, 15 mmol) in DMF (ca. 100 mL) at 50 °C for 1 h yielded the colorless resin. IR (KBr): $\tilde{\nu}$ = 3485 (m, ν_{as}(N–H)), 3388 (m, ν_s(N–H)), 3081 (m), 3058 (m), 3024 (m, ν_{Ar}(C–H)), 2925 (s, $\nu(CH_2)$), 2850 (s, $\nu(CH_2)$), 1944 (m), 1873 (m), 1804 (m), 1701 (s, ν(C=O)), 1618 (m, δ(N–H)), 1598 (s, ν_{Ar}(C=C)), 1444 (m, δ(C–H)), 1070 (s, ν(C–O)), 840 (m), 744 (s), 693 cm^{-1} (s). elemental analysis calcd (%) for $C_{85}H_{85}NO_2$ (1151): C 88.62, H 7.38, N 1.22; found: C 87.28, H 7.36, N 0.91; loading: 75 %.

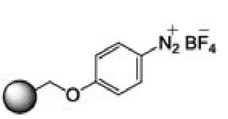


(2-Amino-5-nitrophenyl)carboxymethylpolystyrene: The procedure described for the preparation of **3** was followed. The reaction starting from Cs_2CO_3 (3.05 g, 9.36 mmol), Merrifield resin (5 g, 4.7 mmol) and 5-nitroanthranilic acid (2.5 g, 14.1 mmol) in DMF (ca. 100 mL) at 50 °C for 1.5 h yielded the colorless resin. IR (KBr): $\tilde{\nu}$ = 3473 (m, ν_{as}(N–H)), 3355 (m, ν_s(N–H)), 3081 (m), 3058 (m), 3023 (m, ν_{Ar}(C–H)), 3002 (m), 2921 (s, $\nu(CH_2)$), 2850 (s, $\nu(CH_2)$), 1944 (m), 1871 (m), 1803 (m), 1697 (s, ν(C=O)), 1597 (s, ν_{Ar}(C=C)), 1449 (m, δ(C–H)), 1321 (s, ν_s(N=O)), 829 (m), 746 (s), 695 cm^{-1}

(s); elemental analysis calcd (%) for $C_{85}H_{84}N_2O_4$ (1196): C 85.28, H 7.02, N 2.34; found: C 86.423, H 7.87, N 1.91; loading: 81 %.

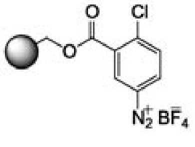


(5-Diazonio-2-chlorophenyl)methyl-1-oxymethylpolystyrene tetrafluoroborate (4): The amine resin (2 g) was suspended in dry THF (50 mL). $BF_3{\cdot}Et_2O$ (0.33 mL) was added, followed after 5 min by *t*BuONO (0.35 mL). After a reaction time of 60 min, the mixture was collected in an inert gas frit, filtered, and washed with chilled THF (4×15 mL g^{-1} resin). The resin was washed on an inert gas frit with solvents (three times with each, ca. 20 mL for each solvent per 1.00 g resin): THF, Et_2O, and MeOH. Subsequently the resin was dried in vacuo. ^{19}F NMR (C_6D_6): δ = -148.3 ppm (s, BF_4^-). IR (KBr): $\tilde{\nu}$ = 3081 (m), 3058 (m), 3021 (m, ν_{Ar}(C−H)), 3002 (m), 2928 (s, ν(CH_2)), 2851 (s, ν(CH_2)), 2278 (s, ν(−N≡N)), 1944 (m), 1872 (m), 1803 (m), 1600 (s, ν_{Ar}(C=C)), 1441 (m, δ(C−H)), 1052 (s, ν(C−O)), 1013 (s, ν(C−Cl)), 842 (m), 820 (m), 741 (s), 692 cm^{-1} (s); elemental analysis calcd (%) for $C_{85}H_{84}N_2OClBF_4$ (1270.5): C 80.28, H 6.61, N 2.20; found: C 83.59, H 6.53, N 1.10; loading: 50 %.

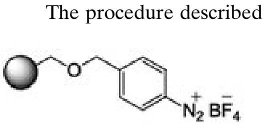


(4-Diazoniophenoxy)methylpolystyrene tetrafluoroborate (8): a) Reaction at room temperature: The procedure described for the preparation of **4** was followed. The reaction starting from amino resin (2 g), $BF_3{\cdot}OEt_2$ (0.33 mL), and *t*BuONO (0.35 mL) in THF (50 mL) at room temperature yielded a dark resin. IR (KBr): $\tilde{\nu}$ = 3102 (m), 3081 (m), 3057 (m), 3022 (m, ν_{Ar}(C−H)), 2924 (s, ν(CH_2)), 2851 (s, ν(CH_2)), 2243 (s, ν(−N≡N)), 1944 (m), 1872 (m), 1803 (m), 1600 (s, ν_{Ar}(C=C)), 1441 (m, δ(C−H)), 1052 (s, ν(C−O)), 1013 (s, ν(C−Cl)), 834 (m), 741 (s), 692 cm^{-1} (s).

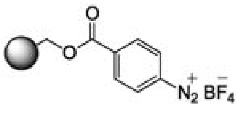
b) Reaction at 0 °C: Similarly, the reaction starting from amino resin (2 g), $BF_3{\cdot}OEt_2$ (0.33 mL), and *t*BuONO (0.35 mL) in THF (50 mL) at 0 °C yielded a dark resin. IR (KBr): $\tilde{\nu}$ = 3081 (m), 3058 (m), 3022 (m, ν_{Ar}(C−H)), 2915 (s, ν(CH_2)), 2849 (s, ν(CH_2)), 2243 (m, ν(N≡N)), 1943 (m), 1872 (m), 1803 (m), 1747 (w), 1598 (s, ν_{Ar}(C=C)), 1449 (m, δ(C−H)), 1067 (s, ν(C−O)), 825 (m), 745 (s), 694 cm^{-1} (s); elemental analysis calcd (%) for $C_{84}H_{83}N_2OBF_4$ (1222): C 82.49, H 6.79, N 2.29; found: C 83.92, H 6.97, N 1.40; loading: 61 %.



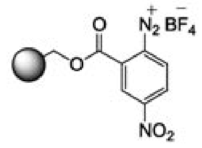
(5-Diazonio-2-chlorophenyl)carboxymethylpolystyrene tetrafluoroborate (10): The procedure described for the preparation of **4** was followed. The reaction starting from amino resin (1 g), $BF_3{\cdot}OEt_2$ (0.33 mL), and *t*BuONO (0.35 mL) in THF (50 mL) at 0 °C for 30 min yielded the orange resin. IR (KBr): $\tilde{\nu}$ = 3081 (m), 3059 (m), 3024 (m, ν_{Ar}(C−H)), 2920 (s, ν(CH_2)), 2850 (s, ν(CH_2)), 2286 (s, ν(−N≡N)), 1944 (m), 1872 (m), 1803 (m), 1736 (s, ν(C=O)), 1601 (s, ν_{Ar}(C=C)), 1451 (m, δ(C−H)), 1052 (s, ν(C−O)), 1013 (s, ν(C−Cl)), 821 (m), 747 (s), 697 cm^{-1} (s); elemental analysis calcd (%) for $C_{85}H_{82}N_2O_2ClBF_4$ (1284): C 79.42, H 6.38, N 2.18; found: C 79.538, H 6.43, N 1.55; loading: 71 %.



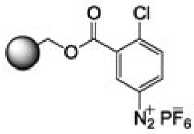
(4-Diazoniophenyl)methyl-1-oxymethylpolystyrene tetrafluoroborate (9): The procedure described for the preparation of **4** was followed. The reaction starting from amino resin (1 g), $BF_3{\cdot}OEt_2$ (0.33 mL), and *t*BuONO (0.35 mL) in THF (50 mL) at 0 °C for 30 min yielded a dark to brownish yellow resin. IR (KBr): $\tilde{\nu}$ = 3081 (m), 3058 (m), 3022 (m, ν_{Ar}(C−H)), 2907 (s, ν(CH_2)), 2850 (s, ν(CH_2)), 2274 (w, ν(−N≡N)), 1944 (m), 1872 (m), 1803 (m), 1599 (s, ν_{Ar}(C=C)), 1442 (m, δ(C−H)), 1060 (s, ν(C−O)), 840 (m), 743 (s), 694 cm^{-1} (s); elemental analysis calcd (%) for $C_{85}H_{85}N_2OBF_4$ (1236): C 82.52, H 6.88, N 2.27; found: C 86.133, H 7.706, N 1.065; loading: 47 %.



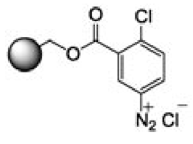
(4-Diazoniophenyl)carboxymethylpolystyrene tetrafluoroborate (6): The procedure described for the preparation of **4** was followed. The reaction starting from amino resin (1 g), $BF_3{\cdot}OEt_2$ (0.33 mL) and *t*BuONO (0.35 mL) in THF (50 mL) at 0 °C for 30 min yielded the light yellow resin. IR (KBr): $\tilde{\nu}$ = 3395 (m, ν(N−H)), 3082 (m), 3059 (m), 3024 (m, ν_{Ar}(C−H)), 3001 (m), 2910 (s, ν(CH_2)), 2852 (s, ν(CH_2)), 2290 (w, ν(−N≡N)), 1943 (m), 1872 (m), 1803 (m), 1709 (s, ν(C=O)), 1601 (s, ν_{Ar}(C=C)), 1450 (m, δ(C−H)), 840 (m), 748 (s), 696 cm^{-1} (s); elemental analysis calcd (%) for $C_{85}H_{83}N_2O_2BF_4$ (1250): C 81.60, H 6.64, N 2.24; found: C 85.72, H 7.95, N 0.048; loading: 2 %.



(2-Diazonio-2-nitrophenyl)carboxymethylpolystyrene tetrafluoroborate (5): The procedure described for the preparation of **4** was followed. The reaction starting from amino resin (1.6 g), $BF_3{\cdot}OEt_2$ (0.4 mL), and *t*BuONO (0.4 mL) in THF (50 mL) at 0 °C for 1.5 h yielded a light yellow resin. IR (KBr): $\tilde{\nu}$ = 3082 (m), 3058 (m), 3022 (m, ν_{Ar}(C−H)), 3001 (m), 2909 (s, ν(CH_2)), 2850 (s, ν(CH_2)), 2306 (m, ν(−N≡N)), 1945 (m), 1872 (m), 1804 (m), 1702 (s, ν(C=O)), 1600 (s, ν_{Ar}(C=C)), 1450 (m, δ(C−H)), 1323 (s, ν_s(N=O)), 841 (m), 746 (s), 693 cm^{-1} (s); elemental analysis calcd (%) for $C_{85}H_{82}N_3O_4BF_4$ (1295): C 78.76, H 6.33, N 3.24; found: C 83.23, H 10.19, N 0.95; loading: 30 %.



(5-Diazonio-2-chlorophenyl)carboxymethylpolystyrene hexafluorophosphate (12): Resin **10** (0.5 g) was added to a saturated solution of KPF_6 (1.38 g, 7.5 mmol) in acetonitrile (6.4 mL). Agitation for 64 h, followed by washing with water and organic solvents, as described above yielded the resin. IR (KBr): $\tilde{\nu}$ = 3081 (m), 3059 (m), 3024 (m, ν_{Ar}(C−H)), 2925 (s, ν(CH_2)), 2851 (s, ν(CH_2)), 2283 (s, ν(−N≡N)), 1945 (m), 1872 (m), 1803 (m), 1736 (s, ν(C=O)), 1601 (s, ν_{Ar}(C=C)), 1450 (m, δ(C−H)), 1026 (s, ν(C−Cl)), 829 (m), 743 (s), 697 cm^{-1} (s). elemental analysis calcd (%) for $C_{85}H_{82}N_2O_2ClPF_6$ (1342.5): C 75.98, H 6.11, N 2.09; found: C 76.503, H 6.92, N 1.10; loading: 53 %.



(5-Diazonio-2-chlorophenyl)carboxymethylpolystyrene chloride (11): The amino resin (1 g) was suspended in dry dichloromethane (ca. 25 mL) and treated with HCl (5 mL, 1 M). After 1 h, the resin was washed on an inert gas frit with solvents (three times with each, ca. 20 mL for each solvent): THF, Et_2O, and MeOH. Subsequently the resin was dried in vacuo. The resin was the suspended in THF and cooled to −20 °C. Isoamylnitrite (0.35 mL) was added, stirred for 1 h at −20 to −10 °C. After 1 h, the resin was washed on an inert gas frit with solvents (three times with each, ca. 20 mL for each solvent): THF, Et_2O, and MeOH. Subsequently the resin was dried in vacuo. IR (KBr): $\tilde{\nu}$ = 3081 (m), 3058 (m), 3022 (m, ν_{Ar}(C−H)), 2903 (s, ν(CH_2)), 2850 (s, ν(CH_2)), 2253 (w, ν(−N≡N)), 2116 (m), 1944 (m), 1872 (m), 1802 (m), 1719 (s, ν(C=O)), 1598 (s, ν_{Ar}(C=C)), 1441 (m, δ(C−H)), 1022 (s, ν(C−Cl)), 816 (m), 739 (s), 694 (s); elemental analysis calcd (%) for $C_{85}H_{82}N_2O_2Cl_2$ (1233): C 82.73, H 6.65, N 2.27; found: C 82.851, H 6.53, N 1.38; loading: 61 %.

Thermal measurements: The thermal measurements were carried out on a Perkin–Elmer DSC 7 with polymer-bound diazonium ions with a loading of 1.0 mmol g^{-1}. The runs were conducted in perforated closed aluminum crucibles containing approximately 10 mg of the sample. An empty crucible was used as the reference. The study was carried out over the temperature range of ambient to 200 °C, at seven heating rates of 1, 3, 5, 7, 10, 15 and 20 K min^{-1}.

The DSC analysis of the used chloromethylpolystyrene resin resulted an endothermic melting enthalpy of $\Delta_M H = 2.6$ J g^{-1} at the melting point of 118 °C. The melting point is in the region of the exothermal decomposition of the diazonium ions, but it is about 50 times smaller. Because the tolerance of the method is at about 10 %, the melting enthalpy was not taken into account for the examination of the reaction enthalpy.

Mathematical methods

Kinetic analysis: The stability of the resins is given by the rate at which the first decomposition step occurs. Therefore we used DSC runs at seven different heating rates for investigating the decomposition reaction occurring around 90–160 °C (Figure 5); the kinetics of this reaction were analyzed with the help of both the iso-conversional differential and inte-

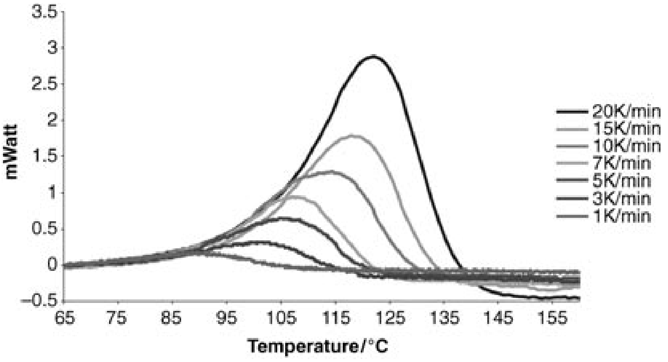


Figure 5. DSC measurements on solid-phase bound diazonium ion **4** at various heating rates.

gral methods as well as the invariant kinetic parameters method, Kissinger method, and a differential isothermal method. All of them led to similar values for the kinetic parameters and indicated that the first-order mechanism fits the data best. The values of the kinetic parameters were further used for calculating the half-life time of the ion at various temperatures. The result of stability prediction at 6 °C was compared with those of an isothermal test monitored analytically, and we noticed a good agreement of the calculated and measured times. As it appears the decomposition process is single step, corresponding to Scheme 4. The methodology was exemplified for resin **4**, but similar approaches were used for the other ones.

The kinetics of the decomposition are described by the known differential relationship given in Equation (1):

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = f(1-\alpha)A\exp\left(-\frac{E}{RT}\right) \tag{1}$$

in which α, the conversion degree, is calculated from the area ratio of the DSC peaks [Eq. (2)]

$$\alpha = \frac{\mathrm{DSC}_t}{\mathrm{DSC}_{\mathrm{Total}}} \tag{2}$$

and the temperature time dependency is given by Equation (3) in which β is the heating rate.

$$T = T_0 + \beta t \tag{3}$$

Eqn. (1) is used also in its integral form [Eq. (4)]

$$\int_{\alpha_i}^{\alpha_j} \frac{\mathrm{d}\alpha}{f(1-\alpha)} = \int_{T_i}^{T_j} \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{4}$$

The left-hand side integral is known as “the conversion integral” and denoted by $g(\alpha)$ and the right-hand side integral is called “the temperature integral” and we denote it by $I(T)$. By considering the heating rate (β) and the parameter A as being temperature independent, Equation (4) can be finally written as Equation (5)

$$g(\alpha) = (A/\beta)\,I(T) \tag{5}$$

Equations (1) and (5) were both used for investigating the thermal stability of the diazonium ion quantitatively.

Our analysis was conducted, in a first step, to find out the so-called “kinetic triplet”; that is, the values of parameters A and E, usually termed as pre-exponential factor and activation energy, respectively, and the analytical form of the kinetic function, $f(1-\alpha)$. In the second part we investigated the possibilities of predicting the thermal stability of our compounds based on the obtained kinetic triplet.

Parameter E: From the recorded data, we first calculated the value of the parameter E by the help of two iso-conversional methods, that is, the differential method of Friedman,[47] and an integral one, which is a variant of those proposed by Flynn–Wall and Ozawa.[48,49]

The differential method is based on Equation (1) written in a logarithmic form [Eq. (6)]

$$\ln(\mathrm{d}\alpha/\mathrm{d}t) = \{(-E/R)(1/T)\} + \ln[A\{f(1-\alpha)\}] \tag{6}$$

The plot of $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ versus $1/T$ for values measured at the same value of α on each of the seven runs is a straight line, the slope of which equals $-E/R$ and the intercept is composed of the value of parameter A and the unknown kinetic function, $f(1\text{-}\alpha)$.

The integral method is based on Equation (5). The method makes use of the first mean theorem of integrals for evaluating the temperature integral $I(T)$[50] [Eq. (7)].

$$I(T) = (T_j - T_i)\exp(-E/RT_\xi) \tag{7}$$

In Equation (7) T_ξ is a temperature value within the interval (T_i, T_j). For temperature intervals of up to 10° the approximation given in Equation (8) is considered good enough[49] and it is used in the present work.

$$T_\xi = (T_i + T_j)/2 \tag{8}$$

With Equation (7), after rearranging and taking the logarithms, Equation (5) can be written in the following form [Eq. (9)]

$$\ln\left(\frac{\beta}{T_j - T_i}\right) = -\frac{E}{R}\frac{1}{T_\xi} + \ln\left(\frac{A}{g(\alpha_j) - g(\alpha_i)}\right) \tag{9}$$

The plot of $\ln[\beta/(T_j-T_i)]$ versus $1/T_\xi$ for values of temperatures measured at the same value of α on each of the seven curves leads to a straight line, the slope of which equals $-E/R$ and the intercept is composed of the value of parameter A and the integral of the unknown kinetic function.

The results, calculated by each of the two methods, are plotted in Figure 6 against the conversion degree.

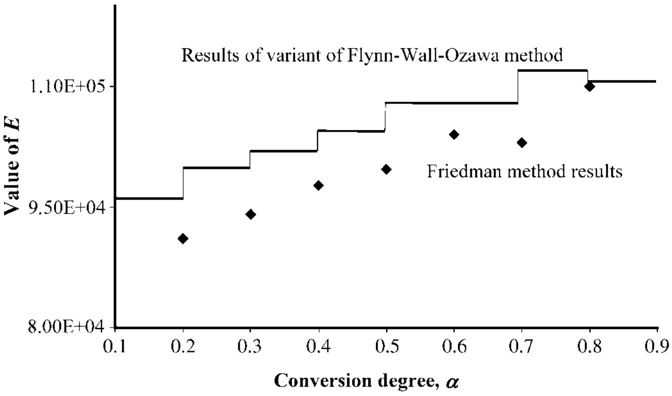


Figure 6. The dependence of kinetic parameter E, as calculated from integral (variant of Flynn–Wall–Ozawa) and differential (Friedman) iso-conversional methods, on the conversion degree (α) of the reaction.

The plots look very similar, the results from the integral method giving slightly higher values than those obtained by the differential one. The stairs plot of the results of the integral method shows the intervals for which the constancy of parameter E was used in applying Equation (7) for the temperature integral. We also note the increase of E with the conversion degree; this might be due to the increasing influence played by the diffusion of produced nitrogen through the newly formed compound. The standard deviations calculated for both cases, and given in Table 5, suggest, however, that the variation of E with the conversion degree is small enough to allow considering the mean values as constants over the whole process.

As the value of parameter E may be considered as quasi-independent of the conversion degree, we calculated the invariant kinetic parameters of the reaction A_i and E_i.[51]

The method is based on the observation that by choosing a different analytical form of the kinetic function, $f(1-\alpha)$, the values of the two parameters E and A, calculated from the data recorded at a single heating rate, are linearly related to each other through a so-called "apparent compensation effect" [Eq. (10)] in which $c1$ and $c2$ are two appropriate constants:[50]

$$\ln(A) = c1E + c2 \tag{10}$$

Similar straight lines are obtained at each heating rate and they were shown to form a pencil, whose coordinates of the crossing point are the values of E_i and A_i, which are named "invariant kinetic parameters" as they no longer depend on the choice of the kinetic function.[50] The values calculated according to this method are also given in Table 5.

Finally, with the peak temperatures (T_{peak}) from DSC curves recorded at different heating rates, the plot of $\ln(\beta/T^2_{\mathrm{peak}})$ versus $1/T_{\mathrm{peak}}$ gives a straight line, the slope of which equals $-E/R$, from which parameter E is easily calculated. This is the Kissinger method[52] and the result (the value of parameter E) is also listed in Table 5.

We note, from Table 5, that all the calculated values of parameter E lie within 10% of each other, no matter which method was used.

The kinetic function, f(1−α): The calculated values of the two invariant kinetic parameters allow the ready selection of the kinetic function, $f(1-\alpha)$, out of a group of functions proposed in literature[53] by using Equation (1) and some statistical criteria, for example, minimizing the sum of residuals. The best result obtained this way indicated the first-order reaction model as the most suitable function for fitting the experimental data.

The analytical form of the kinetic function $f(1-\alpha)$ was also determined by using an average iso-conversional value for parameter E in a method described previously by Malek.[54] According to this, Equation (1) can be rewritten as Equation (11).

$$\frac{d\alpha}{dt}/\exp(-E_i/RT) = A_i\{f(1-\alpha)\} \tag{11}$$

By substituting Equation (2) into Equation (11) and dividing both sides with the maximum values in order to normalize them, one obtains, after simplifying the constants $\mathrm{DSC_{Total}}$ and A_i, Equation (12).

$$G(t) = \frac{\mathrm{DSC}_t/\exp(-\mathrm{E_i}/RT)}{\max[\mathrm{DSC}_t/\exp(-E_i/RT)]} = \frac{f(1-\alpha)}{\max[f(1-\alpha)]} \tag{12}$$

By this operation we obtain a left-hand side function, $G(t)$, ranging from 0 to 1, built out of only experimental data and the value of E. This function has to be fitted by the right-hand side function, which is the normalized kinetic function only, as A vanishes through division. The kinetic function $f(1-\alpha)$ should have the general form given in Equation (13), and a nonlinear estimation program was used for finding the best values of a and b for fitting the curve $G(t)$. For the seven different heating rates we obtained $a = 0 \pm 0.09$ and $b = 0.9 \pm 0.13$.

$$f(1-\alpha) = \alpha^a(1-\alpha)^b \tag{13}$$

As it appears both from the invariant kinetic method and from this approach, the reaction order models best the experimental data. While the 0.9 value of the reaction order has no physical meaning, we may expect, from the dediazonation mechanism proposed, first-order kinetics to occur. Consequently we have taken the kinetic function as Equation (14)

$$f(1\text{-}\alpha) = 1-\alpha \tag{14}$$

The parameter A: The parameter A was calculated as a scaling parameter, by dividing the left-hand term of Equation (4) by the kinetic function obtained above, and taking the mean value. For the seven plots we have obtained $\ln(A) = 30.24 \pm 1.2\ \mathrm{min^{-1}}$, a value close to those obtained from the invariant kinetic parameter method above (see Table 5).

The validation of the calculated parameters: Within the framework of the reaction order model, Equation (1) can be rewritten as Equation 15 in which n is the reaction order and $k(T) = A\exp(-E/RT)$.

$$\ln(d\alpha/dt) = n\ln(1-\alpha) + \ln[k(T)] \tag{15}$$

Taking the experimental values of $d\alpha/dt$ and of the conversion degree (α) at the same temperature (T) on all the seven DSC curves, a plot of $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$ gives a straight line, the slope of which equals the reaction order (n) and the intercept is the logarithm of the rate constant. The values of the intercept at several temperatures allows, then, calculation of the parameters E and A as the slope and the intercept, respectively, of the plot $\ln[k(T)]$ versus $1/T$.

This procedure, which is similar to an isothermal approach,[52] can be followed also for a more general kinetic function, as those given by Equation (13), by using the nonlinear regression.

The results obtained from this "isothermal" method are also close to all the other results and are listed in Table 5.

Comparing the reproduction of the experimental data with the calculated parameters provides further evidence for the validity of the obtained values. The result is shown in Figure 7 for one heating rate (5 K min^{-1}) and the use of the invariant kinetic parameters; a fairly good reproducibility of the initial DSC signal is noted.

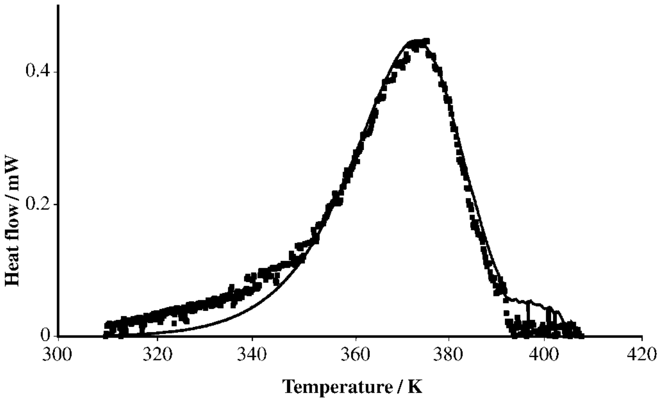


Figure 7. Reconstruction of the experimental DSC curves with the calculated parameters (full line is the reconstructed DSC curve, and the dots are the experimental recorded points).

Lifetime prediction: The results of the kinetic analysis were further used for predicting the half-life time of the synthesized product. We used the first-order kinetic model and the parameters E and A, taken from Table 5, in Equation (16), obtained by integrating Equation (1) for α going from 0 to 0.5 under isothermal conditions.

$$t_{1/2} = \frac{\ln(2)}{A}\exp\left(\frac{E}{RT}\right) \tag{16}$$

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