

Kinetic and Mechanistic Study on *p*-Quinodimethane Formation in the Sulfinyl Precursor Route for the Polymerization of Poly(*p*-phenylenevinylene) (PPV)

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SUPPORTING INFORMATION: Cartesian coordinates of B3LYP/6-31+G(d,p) optimized geometries of all reactants, transition states and products; imaginary and low frequency modes of transition states; experimental set-up of the UV-vis stop flow accessory.

TABLE 1: Cartesian coordinates (B3LYP/6-31+G(d,p)) of reactants corresponding to deprotonation reaction of monomer **1** by *tert*-butoxide in gas phase.

TABLE 2: Cartesian coordinates (B3LYP/6-31+G(d,p)) of reactants corresponding to deprotonation reaction of monomer **2** by *tert*-butoxide in gas phase.

TABLE 3: Cartesian coordinates (B3LYP/6-31+G(d,p)) of reactants corresponding to deprotonation reaction of monomer **3** by *tert*-butoxide in gas phase.

TABLE 4: Cartesian coordinates, imaginary and low frequency modes (B3LYP/6-31+G(d,p)) of transition state corresponding to deprotonation reaction of monomer **1** by *tert*-butoxide in gas phase.

TABLE 5: Cartesian coordinates, imaginary and low frequency modes (B3LYP/6-31+G(d,p)) of transition state corresponding to deprotonation reaction of monomer **2** by *tert*-butoxide in gas phase.

TABLE 6: Cartesian coordinates, imaginary and low frequency modes (B3LYP/6-31+G(d,p)) of transition state corresponding to deprotonation reaction of monomer **3** by *tert*-butoxide in gas phase.

TABLE 7: Cartesian coordinates (B3LYP/6-31+G(d,p)) of products corresponding to deprotonation reaction of monomer **1** by *tert*-butoxide in gas phase.

TABLE 8: Cartesian coordinates (B3LYP/6-31+G(d,p)) of products corresponding to deprotonation reaction of monomer **2** by *tert*-butoxide in gas phase.

TABLE 9: Cartesian coordinates (B3LYP/6-31+G(d,p)) of products corresponding to deprotonation reaction of monomer **3** by *tert*-butoxide in gas phase.

TABLE 10: Cartesian coordinates (B3LYP/6-31+G(d,p)) of solvated reactants corresponding to deprotonation reaction of monomer **2** by *tert*-butoxide.

TABLE 11: Cartesian coordinates (B3LYP/6-31+G(d,p)) of solvated transition state corresponding to deprotonation reaction of monomer **2** by *tert*-butoxide.

TABLE 12: Cartesian coordinates (B3LYP/6-31+G(d,p)) of solvated products corresponding to deprotonation reaction of monomer **2** by *tert*-butoxide.

FIGURE S1: Principle and experimental set-up of the UV-vis stop flow accessory.

TABLE 1: Cartesian coordinates (B3LYP/6-31+G(d,p)) of reactants corresponding to deprotonation reaction of monomer **1** by *tert*-butoxide in gas phase.

C	1.12106400	-0.43490300	-0.13758800
C	2.59402900	-0.33552500	-0.36625000
C	3.20180500	-0.92721400	-1.48741900
C	4.56922800	-0.79592500	-1.72324900
C	5.37979200	-0.07678900	-0.83256200
C	4.78061000	0.50079700	0.29814500
C	3.41192700	0.38077000	0.52759500
S	0.71357200	-1.54750000	1.32142700
O	1.55162200	-1.09720000	2.52182500
C	-0.99422800	-0.90734800	1.61001300
C	-1.99492500	-1.35663300	0.54429300
C	-3.42081000	-0.90807100	0.89687000
C	-4.45379100	-1.28389300	-0.17344200
C	-5.88355000	-0.84852300	0.17508600
C	-6.91557300	-1.19143800	-0.90750800
C	-8.34653600	-0.76153100	-0.55727100
C	-9.36936000	-1.09947000	-1.64877200
C	6.83703200	0.09776300	-1.09661100
Cl	7.89038200	-1.28967100	-0.43029600
H	0.62008100	0.54467700	0.04823300
H	0.62616400	-0.91361300	-0.98934800
H	2.58757200	-1.48348100	-2.19144700
H	5.01267100	-1.25510700	-2.60432200
H	5.39447800	1.05713500	1.00312200
H	2.95979200	0.83079600	1.40404900
H	-0.93405800	0.19118700	1.62774500
H	-1.24255100	-1.31166900	2.59885700
H	-1.97093900	-2.45010600	0.41583000
H	-1.72159300	-0.89484600	-0.41060000
H	-3.40797800	0.18049100	1.02929200
H	-3.71825100	-1.34879900	1.86098300
H	-4.15948800	-0.82402600	-1.12747900
H	-4.43748600	-2.37261000	-0.33756700
H	-5.89385900	0.23583200	0.35467500
H	-6.18495800	-1.31798600	1.12367500
H	-6.61823600	-0.71541700	-1.85346100
H	-6.90089600	-2.27583400	-1.09518100
H	-8.36051800	0.32045000	-0.36633400
H	-8.64705700	-1.24034100	0.38548300
H	-10.37955600	-0.77874900	-1.36856300
H	-9.11406500	-0.60699700	-2.59498000
H	-9.40325300	-2.17944100	-1.83872400
H	7.23942700	0.99000800	-0.61753300
H	7.06885500	0.11234400	-2.16158300
C	-0.94814700	3.10950200	0.09061000
C	-2.39353900	3.58181500	0.43864100
C	-0.66390900	3.49832900	-1.39345200
O	-0.82148500	1.76086500	0.27833600
C	0.04471000	3.90298200	0.99430300
H	-2.61405400	3.32866500	1.48300700
H	-3.11015900	3.04587300	-0.19633700
H	-2.54511500	4.66437700	0.30097200
H	-1.36089800	2.95897800	-2.04704200
H	0.35388300	3.18883100	-1.66117700
H	-0.76316500	4.57810700	-1.58889900
H	-0.03413800	4.99543700	0.87459400
H	1.07228300	3.60119900	0.75711200
H	-0.14268300	3.65154500	2.04525500

TABLE 2: Cartesian coordinates (B3LYP/6-31+G(d,p)) of reactants corresponding to deprotonation reaction of monomer **2** by *tert*-butoxide in gas phase.

C	0.44279700	-0.35161300	-0.09227500
C	1.91373000	-0.22488100	-0.31302600
C	2.55327300	-0.88228600	-1.37901500
C	3.91689900	-0.72163900	-1.61369400
C	4.69041300	0.09986100	-0.78014300
C	4.06183900	0.73611400	0.30253500
C	2.69740900	0.58388900	0.53218000
S	0.05160100	-1.37415300	1.43707400
O	0.86756600	-0.82122800	2.60912300
C	-1.67496200	-0.76005000	1.66662100
C	-2.65257500	-1.32571200	0.63544300
C	-4.08834000	-0.85536200	0.91052100
C	-5.10016700	-1.37658600	-0.11830700
C	-6.53673100	-0.90160000	0.13706400
C	-7.54814800	-1.41065900	-0.89862100
C	-8.98508200	-0.93399700	-0.64879800
C	-9.98712400	-1.44643700	-1.69047900
C	6.10923800	0.38417100	-1.10384700
H	-0.08491800	0.62556200	0.02665000
H	-0.02904900	-0.90104800	-0.91394500
H	1.96527100	-1.51151900	-2.04284100
H	4.38457200	-1.22412800	-2.45775900
H	4.64767200	1.37422500	0.96041100
H	2.22021300	1.08357700	1.36745600
H	-1.64324600	0.33828300	1.59584700
H	-1.91999900	-1.09015300	2.68333600
H	-2.61754100	-2.42630000	0.62233100
H	-2.36479600	-0.96813800	-0.35950200
H	-4.08925400	0.24129400	0.90824900
H	-4.39538800	-1.17710600	1.91763500
H	-4.78700200	-1.05225600	-1.12108800
H	-5.08008200	-2.47750500	-0.13072700
H	-6.55390200	0.19733500	0.15094100
H	-6.85349700	-1.22426800	1.14037100
H	-7.23131000	-1.08834400	-1.90153000
H	-7.53088900	-2.51105100	-0.91389700
H	-9.00285100	0.16459100	-0.63491100
H	-9.30383100	-1.25550700	0.35295400
H	-11.00321300	-1.09177100	-1.48163300
H	-9.71702100	-1.10811800	-2.69826600
H	-10.01366800	-2.54305600	-1.70774800
H	6.45404900	1.34119800	-0.71706800
H	6.33288000	0.30629900	-2.16630300
C	-1.63314900	3.18724800	0.01331700
C	-3.06783300	3.67973800	0.37601700
C	-1.35909500	3.56917500	-1.47410000
O	-1.52381300	1.83664100	0.20231300
C	-0.61964500	3.96744800	0.90522900
H	-3.28020600	3.43288200	1.42354400
H	-3.79857000	3.15157100	-0.24923100
H	-3.20630100	4.76380100	0.23664800
H	-2.07078800	3.03947800	-2.11960000
H	-0.34889600	3.24429800	-1.75216300
H	-1.44434700	4.65005700	-1.66986500
H	-0.68520800	5.06071900	0.78563400
H	0.40127600	3.65236800	0.65669500
H	-0.79830800	3.71914900	1.95839900
Br	7.40217200	-0.94212000	-0.26952700

TABLE 3: Cartesian coordinates (B3LYP/6-31+G(d,p)) of reactants corresponding to deprotonation reaction of monomer **3** by *tert*-butoxide in gas phase.

C	-1.52989200	0.18598000	1.28197900
C	-2.91791400	-0.03009200	0.76154400
C	-3.92545300	-0.58449900	1.56654800
C	-5.22553900	-0.73476200	1.08613500
C	-5.55341700	-0.34081200	-0.21936000
C	-4.54332800	0.19896100	-1.03083600
C	-3.24569200	0.35522300	-0.54904900
C	-6.95364100	-0.46028100	-0.72329400
Cl	-7.33055500	-2.11048600	-1.49473200
H	-1.05431000	1.11888200	0.88929500
H	-1.50184500	0.18422600	2.37496400
H	-3.68471600	-0.89598700	2.57934000
H	-5.99279500	-1.16234000	1.72792900
H	-4.77924200	0.50713600	-2.04692200
H	-2.47286000	0.78607000	-1.17692500
H	-7.16987100	0.26022400	-1.51190900
H	-7.69009200	-0.36672400	0.07488500
C	0.25346400	3.63955800	-0.11091700
C	1.72955100	4.06951800	-0.36720300
C	-0.35984200	4.62402500	0.93088200
O	0.19779900	2.34988400	0.34360100
C	-0.53229400	3.79971600	-1.44763200
H	2.17673100	3.40200700	-1.11421100
H	2.30111700	3.96453500	0.56321700
H	1.82598800	5.10725900	-0.72363000
H	0.18625200	4.53242800	1.87780200
H	-1.40485500	4.34792500	1.11865800
H	-0.32928800	5.67674200	0.60766200
H	-0.49804100	4.82309500	-1.85400400
H	-1.58281300	3.52671800	-1.28720500
H	-0.11708300	3.11231200	-2.19454700
S	-0.38036500	-1.16760000	0.79585300
C	1.24661200	-0.38098300	1.01411600
O	-0.51398300	-2.28568200	1.77152200
O	-0.56875900	-1.47701600	-0.64177300
C	2.35189100	-1.18703900	0.33125400
H	1.39261000	-0.32677400	2.09831900
H	1.13550900	0.64339200	0.61246100
H	2.12806100	-1.25619200	-0.73925500
H	2.37555100	-2.21376200	0.72041200
C	3.72408000	-0.52623700	0.53215400
H	3.68149000	0.50769600	0.16547100
H	3.94493700	-0.46172200	1.60789100
C	4.86267200	-1.27579800	-0.17253500
H	4.64464500	-1.33274300	-1.24884400
H	4.89353300	-2.31496100	0.18757400
C	6.23969200	-0.62928900	0.02998300
H	6.20499100	0.41129400	-0.32346300
H	6.46038500	-0.57720600	1.10651000
C	7.37996600	-1.36771400	-0.68350000
H	7.41532100	-2.40950500	-0.33127100
H	7.16068800	-1.41894300	-1.76027300
C	8.75717700	-0.72145400	-0.48159700
H	8.72207900	0.31900500	-0.83337300
H	8.97809300	-0.67101600	0.59391500
C	9.89008200	-1.46442200	-1.19994600
H	10.85900500	-0.97921900	-1.03444000
H	9.97089500	-2.49957500	-0.84612400
H	9.71569000	-1.49946500	-2.28226400

TABLE 4: Cartesian coordinates, imaginary and low frequency modes (B3LYP/6-31+G(d,p)) of transition state corresponding to deprotonation reaction of monomer **1** by *tert*-butoxide in gas phase.

C	0.90006000	-0.43959000	0.19320300
C	2.34714200	-0.45822300	-0.09001200
C	2.80392400	-0.66777700	-1.41467300
C	4.14978300	-0.57696100	-1.74999700
C	5.12042800	-0.28973200	-0.77447000
C	4.67973100	-0.09813100	0.54804500
C	3.33286000	-0.16589200	0.88623300
S	0.37247600	-1.36437400	1.69513800
O	1.10575900	-0.82228600	2.93165900
C	-1.34088900	-0.67123600	1.81881900
C	-2.28194300	-1.10426800	0.69470400
C	-3.72675900	-0.64736100	0.94867400
C	-4.69635600	-1.04968200	-0.17064600
C	-6.13931800	-0.58603600	0.06967400
C	-7.11182900	-0.98598500	-1.04783900
C	-8.55367300	-0.51727600	-0.81093900
C	-9.51814200	-0.92111900	-1.93265600
C	6.55242000	-0.17193900	-1.13084100
Cl	7.50946000	-1.80823000	-1.05876400
H	0.35154000	-0.93629000	-0.61856400
H	0.36112800	0.76540800	0.22874400
H	2.07544800	-0.89120800	-2.19073700
H	4.45842200	-0.73937800	-2.78135100
H	5.41071700	0.11984600	1.32486100
H	3.01412800	-0.00269900	1.91001500
H	-1.22651400	0.41733300	1.84250600
H	-1.68021000	-1.04161800	2.79366000
H	-2.26184500	-2.19856700	0.57826900
H	-1.93678400	-0.66366900	-0.24695000
H	-3.73404900	0.44467200	1.06207200
H	-4.08215700	-1.06452800	1.90313200
H	-4.33642800	-0.63369200	-1.12245900
H	-4.68285200	-2.14371400	-0.28965500
H	-6.15125400	0.50740600	0.18538500
H	-6.49888700	-0.99704700	1.02500400
H	-6.75216600	-0.57717700	-2.00361500
H	-7.10264800	-2.08024800	-1.16323000
H	-8.56313000	0.57570500	-0.69737000
H	-8.91419600	-0.92483500	0.14422300
H	-10.53811600	-0.57310200	-1.73220200
H	-9.20474400	-0.49773800	-2.89464000
H	-9.55472100	-2.01126000	-2.04926500
H	7.10961500	0.46424700	-0.44414700
H	6.71111600	0.15160800	-2.15903400
C	0.11972500	3.06623000	-0.01719000
C	-1.01857300	4.11390700	-0.00191900
C	0.82647800	3.11865200	-1.39749100
O	-0.44128300	1.81030800	0.20738100
C	1.14430700	3.42445200	1.08972500
H	-1.52823200	4.08884600	0.96828600
H	-1.75516900	3.86793000	-0.77587300
H	-0.64996900	5.13525300	-0.17847900
H	0.10825500	2.86382400	-2.18617700
H	1.64131200	2.38700700	-1.43350300
H	1.24697300	4.11143300	-1.61507000
H	1.56946200	4.42991200	0.95480900
H	1.96716300	2.70142500	1.09358700
H	0.65629800	3.37841200	2.06980900

Frequencies --	-1012.6653	7.1246	16.4537
Frequencies --	18.9619	23.2575	27.5872
Frequencies --	29.6675	39.1864	41.6191

TABLE 5: Cartesian coordinates, imaginary and low frequency modes (B3LYP/6-31+G(d,p)) of transition state corresponding to deprotonation reaction of monomer **2** by *tert*-butoxide in gas phase.

C	0.26981900	-0.29279900	0.31064300
C	1.72238800	-0.24418600	0.06892800
C	2.23164900	-0.50998500	-1.22685600
C	3.57854400	-0.36047000	-1.52987400
C	4.49688600	0.05804600	-0.55043500
C	4.00639000	0.29673500	0.74742000
C	2.65802300	0.16410200	1.05365200
S	-0.25341300	-1.17932900	1.83944800
O	0.43518200	-0.56578500	3.06740200
C	-1.99408400	-0.55034800	1.90220600
C	-2.88303500	-1.05178300	0.76399700
C	-4.35809300	-0.67995500	0.97936400
C	-5.27040100	-1.13540100	-0.16742500
C	-6.74628300	-0.76736100	0.03540900
C	-7.65808500	-1.21635100	-1.11426300
C	-9.13449400	-0.84890100	-0.91449500
C	-10.03634300	-1.30048700	-2.06961100
C	5.89901000	0.33347500	-0.89556400
H	-0.32401000	0.87742500	0.28564000
H	-0.22804400	-0.85254700	-0.49248100
H	1.54195300	-0.82624500	-2.00601000
H	3.92874800	-0.56167600	-2.54073700
H	4.69812700	0.61596700	1.52499200
H	2.29813100	0.36747300	2.05631600
H	-1.92398000	0.54208700	1.89870300
H	-2.34527300	-0.90891000	2.87734900
H	-2.79580400	-2.14437700	0.66231100
H	-2.54173500	-0.60103500	-0.17406600
H	-4.43258400	0.40963600	1.09256600
H	-4.71439600	-1.11904600	1.92357300
H	-4.91229700	-0.69066500	-1.10674200
H	-5.18348100	-2.22546800	-0.29168800
H	-6.83207200	0.32173000	0.16072000
H	-7.10576100	-1.21134700	0.97587700
H	-7.29987700	-0.77160000	-2.05436600
H	-7.57189200	-2.30587100	-1.24188500
H	-9.22143700	0.23928100	-0.78783100
H	-9.49405100	-1.29358400	0.02428200
H	-11.08268100	-1.02330400	-1.89641900
H	-9.72329100	-0.84435200	-3.01661800
H	-9.99702100	-2.38894100	-2.19985800
H	6.38615000	1.04659000	-0.23408600
H	6.05523500	0.60667300	-1.93696000
C	-0.68441000	3.14417400	-0.13700900
C	-1.87150400	4.13539600	-0.18412500
C	-0.01273000	3.10456500	-1.53536000
O	-1.17861900	1.88947700	0.21330700
C	0.34729900	3.64749400	0.90506900
H	-2.35794800	4.17263800	0.79748300
H	-2.61176500	3.78730400	-0.91414300
H	-1.55752900	5.15317700	-0.45920800
H	-0.73553600	2.74552000	-2.27792000
H	0.83694300	2.41278400	-1.52800400
H	0.35259200	4.09226100	-1.85262500
H	0.72402200	4.65323200	0.66736400
H	1.20163200	2.96348100	0.95316900
H	-0.11615700	3.67244700	1.89785100
Br	7.13496900	-1.31962200	-0.71752600

Frequencies --	-969.5156	7.6663	11.8142
Frequencies --	18.0892	20.6743	23.4416
Frequencies --	35.0569	39.8047	44.0187

TABLE 6: Cartesian coordinates, imaginary and low frequency modes (B3LYP/6-31+G(d,p)) of transition state corresponding to deprotonation reaction of monomer **3** by *tert*-butoxide in gas phase.

C	-1.26521900	0.03959800	0.93628300
C	-2.66272400	-0.23427200	0.52028500
C	-3.69838900	-0.17385800	1.47782900
C	-5.03660100	-0.29746200	1.11575700
C	-5.40345200	-0.50418700	-0.22325700
C	-4.37745000	-0.58419300	-1.18051400
C	-3.03969400	-0.44359300	-0.82567000
C	-6.83168300	-0.60533800	-0.61967500
Cl	-7.52116000	-2.35354000	-0.56585400
H	-1.17524500	0.03854600	2.02755300
H	-0.82801500	1.18696100	0.54287200
H	-3.44050700	-0.01797600	2.52225300
H	-5.80775500	-0.24054200	1.88164500
H	-4.63502500	-0.74826100	-2.22510300
H	-2.26622600	-0.50131500	-1.58228600
H	-7.00234000	-0.29822600	-1.65110000
H	-7.49323000	-0.05462900	0.04863500
C	-0.83004200	3.47705800	-0.12431800
C	0.17804600	4.65029200	-0.19726500
C	-1.93974500	3.83986200	0.89908900
O	-0.14602900	2.33237000	0.26743000
C	-1.47769700	3.29100100	-1.52176700
H	0.97231600	4.40660300	-0.91254500
H	0.64317000	4.79565500	0.78482600
H	-0.29579000	5.59394500	-0.50627900
H	-1.49270500	3.96737900	1.89225900
H	-2.67665600	3.03077800	0.96003500
H	-2.47045400	4.76577500	0.63303600
H	-1.99471800	4.19758800	-1.86981100
H	-2.20415900	2.47107200	-1.49401100
H	-0.70318500	3.02826000	-2.25161900
S	-0.02548500	-1.15160500	0.39874400
C	1.52447700	-0.22630400	0.66913600
C	2.73145600	-1.00421800	0.14618000
H	2.59901700	-1.18780900	-0.92660400
H	2.77755000	-1.98606900	0.63399900
C	4.04514300	-0.24487600	0.38414800
H	3.98799400	0.74078400	-0.09819100
H	4.16604600	-0.05161800	1.46021100
C	5.27870800	-0.99651600	-0.13412100
H	5.16058700	-1.18577900	-1.21096600
H	5.32768600	-1.98553000	0.34478500
C	6.59894300	-0.25236300	0.10689800
H	6.55050200	0.73569200	-0.37376100
H	6.71500400	-0.06053400	1.18389900
C	7.83405900	-1.00411800	-0.40701800
H	7.88263500	-1.99274600	0.07322600
H	7.71984900	-1.19574600	-1.48423900
C	9.15537900	-0.26219100	-0.16530400
H	9.10884600	0.72437100	-0.64736500
H	9.26920900	-0.06909200	0.91071000
C	10.38398500	-1.02254400	-0.67898700
H	11.30962500	-0.46613600	-0.49153900
H	10.47760600	-1.99965700	-0.18950700
H	10.31546800	-1.20092000	-1.75904000
H	1.58423200	-0.06395500	1.75045300
H	1.38002400	0.74375800	0.18168100
O	0.01632600	-2.34168300	1.29684000
O	-0.14515800	-1.40761400	-1.06236500

Frequencies --	-767.2176	6.6205	10.5406
Frequencies --	19.4963	23.3681	28.4441
Frequencies --	32.2898	35.3869	42.2881

TABLE 7: Cartesian coordinates (B3LYP/6-31+G(d,p)) of products corresponding to deprotonation reaction of monomer **1** by *tert*-butoxide in gas phase.

C	1.15392100	-0.14143300	0.13022700
C	1.81913200	1.09975900	0.08884200
C	2.18662400	1.74600200	1.30162800
C	2.81481000	2.96709200	1.32165300
C	3.13969400	3.65057500	0.14488900
C	2.78423400	3.02964200	-1.05839900
C	2.15744400	1.80846500	-1.09729600
S	0.76963900	-1.03128200	-1.26047900
O	1.53810400	-2.36205600	-1.37472800
C	-0.88882000	-1.62569300	-0.83379900
C	-1.92008300	-0.52194000	-0.75335300
C	-3.30224300	-1.03933900	-0.38637300
C	-4.34390300	0.06292200	-0.28991500
C	-5.72814600	-0.44212300	0.08121800
C	-6.76657500	0.66155500	0.19132700
C	-8.15197100	0.15823000	0.56117200
C	-9.17978000	1.27021900	0.67530900
C	3.81695400	4.94777700	0.17039700
Cl	2.60740865	6.52584882	0.23704183
H	1.01061100	-0.63945100	1.08100700
H	1.47859000	-3.67253300	-0.28169600
H	1.96300000	1.24867200	2.23569500
H	3.06714800	3.41205900	2.27693300
H	3.01499600	3.52646700	-1.99336900
H	1.91858700	1.37020400	-2.05495000
H	-0.78803900	-2.16016600	0.11179000
H	-1.13536900	-2.35637300	-1.60320200
H	-1.96947400	0.00080000	-1.71145800
H	-1.58685100	0.21313900	-0.01981100
H	-3.24693800	-1.56826400	0.56860300
H	-3.62577100	-1.77938500	-1.12346900
H	-4.01774100	0.80070000	0.44724100
H	-4.39676800	0.59419400	-1.24393300
H	-5.67227000	-0.98031500	1.03131000
H	-6.05689200	-1.17470800	-0.66108800
H	-6.43858500	1.39240700	0.93520000
H	-6.82164300	1.20256200	-0.75727200
H	-8.09568400	-0.38494200	1.50711800
H	-8.48136100	-0.56860700	-0.18474200
H	-10.16283400	0.88337300	0.94039000
H	-8.89135900	1.99327800	1.43797300
H	-9.27912100	1.81064300	-0.26598200
H	4.40208900	5.13588400	-0.72250600
H	4.43275200	5.08556700	1.05179000
C	2.90046800	-4.68743300	0.58281800
C	2.94885300	-5.93941900	1.44188500
C	3.50052400	-3.50411700	1.33504600
O	1.54238900	-4.44888000	0.31607700
C	3.65352400	-4.90955500	-0.72495700
H	2.50106200	-6.77631600	0.90779900
H	2.38423700	-5.78267600	2.35989100
H	3.97489700	-6.19882800	1.70289400
H	2.96272200	-3.34675000	2.26925000
H	3.41167700	-2.59903900	0.73727200
H	4.55394000	-3.67058800	1.56500700
H	4.71210100	-5.10401400	-0.54688100
H	3.55822100	-4.02847300	-1.35706100
H	3.22772400	-5.75891800	-1.25816500

TABLE 8: Cartesian coordinates (B3LYP/6-31+G(d,p)) of products corresponding to deprotonation reaction of monomer **2** by *tert*-butoxide in gas phase.

C	0.15428100	-1.24735900	0.19764900
C	1.52836500	-0.97930500	0.12303600
C	2.28949200	-0.82304900	1.33877400
C	3.63139500	-0.53269400	1.32955100
C	4.36487100	-0.39431900	0.11619200
C	3.61790600	-0.52087000	-1.09071600
C	2.27499200	-0.80851500	-1.09924000
S	-0.84814900	-1.51492100	-1.19185200
O	-1.43574800	-2.96063600	-1.21687600
C	-2.32855400	-0.51246500	-0.71152600
C	-2.07364600	0.99310500	-0.69728500
C	-3.32628900	1.79827600	-0.31802700
C	-3.08726900	3.31410100	-0.29145800
C	-4.33318800	4.12523000	0.08869800
C	-4.09507900	5.64067900	0.12630700
C	-5.34095400	6.45214300	0.50596100
C	-5.09287700	7.96475700	0.54725500
C	5.77232100	-0.22365500	0.10971500
H	-2.59512600	-3.62101100	-0.08562200
H	-0.31873500	-1.41461100	1.16353300
H	1.76942800	-0.93960500	2.28680500
H	4.16076400	-0.42242600	2.27434100
H	4.14031100	-0.40209200	-2.03838000
H	1.75868400	-0.91353100	-2.04827700
H	-2.64560500	-0.88916700	0.26793900
H	-3.09332500	-0.79026900	-1.44465400
H	-1.72024600	1.31510500	-1.68667900
H	-1.26305600	1.21299700	0.00790200
H	-3.68247800	1.47016200	0.66905400
H	-4.13711100	1.57071800	-1.02548900
H	-2.27724100	3.53964500	0.41662200
H	-2.72790900	3.64210600	-1.27771500
H	-4.69543600	3.79201700	1.07239900
H	-5.14165700	3.90318700	-0.62364100
H	-3.28834400	5.86330200	0.83985500
H	-3.73132900	5.97588300	-0.85620200
H	-5.70575400	6.11519200	1.48644100
H	-6.14638600	6.23341500	-0.20928800
H	-6.00101200	8.51414600	0.82073900
H	-4.31681900	8.21829800	1.27945300
H	-4.75883000	8.33771000	-0.42853100
H	6.30624600	-0.45892300	-0.80389600
H	6.31606200	-0.47288300	1.01377500
C	-2.96960600	-5.46745500	0.51965100
C	-4.04186200	-6.10192800	1.41367000
C	-1.56508900	-5.71343300	1.10285600
O	-3.25203800	-4.06792300	0.50656300
C	-3.05684400	-6.03002600	-0.91206900
H	-5.03910100	-5.90340200	1.00569900
H	-3.99505900	-5.67255100	2.42044300
H	-3.90304000	-7.18700800	1.48903800
H	-1.50397200	-5.30536300	2.11777200
H	-0.80960000	-5.21312000	0.48896700
H	-1.33039700	-6.78498000	1.14334400
H	-2.85658000	-7.10916900	-0.93098500
H	-2.32891700	-5.52762100	-1.55723500
H	-4.05707100	-5.85346100	-1.32330700
Br	6.47877400	2.00129200	0.12668400

TABLE 9: Cartesian coordinates (B3LYP/6-31+G(d,p)) of products corresponding to deprotonation reaction of monomer **3** by *tert*-butoxide in gas phase.

C	2.01833500	0.17775100	1.89401700
C	2.98628800	-0.49529000	1.10820500
C	4.14613700	-1.03975600	1.75376300
C	5.12009600	-1.72909000	1.05885000
C	5.02687800	-1.94480500	-0.33593000
C	3.90410000	-1.38790500	-0.98904000
C	2.91969400	-0.69205500	-0.30990800
S	0.48560200	0.71508000	1.38650600
O	0.52241800	1.32366200	0.01295500
C	-0.61195000	-0.74946400	1.18087400
C	-2.00830300	-0.38475100	0.67802000
C	-2.92784000	-1.60884100	0.55262900
C	-4.33938200	-1.25172700	0.06738400
C	-5.27493400	-2.46124600	-0.05881100
C	-6.68634400	-2.09977700	-0.54004100
C	-7.62805700	-3.30497700	-0.66165700
C	-9.03617000	-2.93217400	-1.14054600
C	6.04404600	-2.69476200	-1.06393200
Cl	7.55966800	-1.61889300	-1.73133900
H	-0.66099600	2.46262400	-0.87044600
H	2.13074500	0.26235200	2.96827100
H	4.24791800	-0.90827300	2.82873500
H	5.98138100	-2.12071800	1.59855200
H	3.81294200	-1.50480400	-2.06813300
H	2.09190000	-0.26000300	-0.86095500
H	-0.64263900	-1.21820600	2.16984300
H	-0.08726200	-1.41939400	0.49093200
H	-1.92174900	0.11641000	-0.29265400
H	-2.45402900	0.34229800	1.36750100
H	-2.99797000	-2.11652000	1.52631700
H	-2.47922500	-2.33622100	-0.14001700
H	-4.78307900	-0.52113300	0.75917300
H	-4.26834500	-0.74324200	-0.90457700
H	-5.34442300	-2.96958400	0.91462000
H	-4.83247000	-3.19200500	-0.75203700
H	-7.12737700	-1.36599200	0.15080600
H	-6.61865500	-1.59471100	-1.51483100
H	-7.69621300	-3.81012200	0.31234100
H	-7.18961400	-4.03797200	-1.35346300
H	-9.68316100	-3.81402000	-1.21362100
H	-9.51365500	-2.22471400	-0.45167700
H	-9.00571900	-2.45878500	-2.12938900
H	5.69402000	-3.13333900	-1.99616700
H	6.58260100	-3.42293800	-0.46064000
C	-1.08329500	4.39580600	-0.79191700
C	-1.90078900	5.32595100	-1.69621800
C	0.40385700	4.79234000	-0.81085000
O	-1.24517300	3.08614700	-1.34974300
C	-1.63035900	4.42377100	0.64706300
H	-2.95031400	5.01167000	-1.70961000
H	-1.52048700	5.28719300	-2.72280800
H	-1.85085900	6.36223300	-1.34191600
H	0.78739100	4.76524000	-1.83675900
H	0.99134600	4.09224600	-0.20895200
H	0.55000700	5.80325300	-0.40979600
H	-1.53983500	5.42641000	1.08517700
H	-1.08771000	3.71812000	1.28405700
H	-2.68911000	4.14027300	0.64830200
O	-0.13492000	1.51872500	2.47813400

TABLE 10: Cartesian coordinates (B3LYP/6-31+G(d,p)) of solvated reactants corresponding to deprotonation reaction of monomer **2** by *tert*-butoxide.

C	0.65283100	-0.24178900	-0.42953000
C	-0.31987100	0.30652600	-1.28055500
C	-1.64119300	-0.13101500	-1.21922200
C	-2.02623400	-1.11974300	-0.30051200
C	-1.05241200	-1.67331000	0.54783900
C	0.27023100	-1.24719300	0.47586600
C	-3.42794200	-1.58338400	-0.24247600
Br	-4.52046700	-0.49727300	1.13819300
C	2.07171100	0.24592000	-0.46917200
S	2.36128200	1.48794400	0.87180400
C	4.11518000	1.88099400	0.49729500
C	4.55447700	3.11641600	1.27863700
O	1.53679400	2.75620400	0.49478100
O	4.35419900	-1.86493800	-0.28276600
C	4.35724000	-3.23073500	-0.58997100
C	5.80590600	-3.72988300	-0.82111500
C	3.52794700	-3.48153300	-1.87213200
C	3.73184200	-4.03650600	0.57463300
O	5.71355100	-0.81323800	1.62567800
C	5.27470000	-1.23629800	2.89170500
O	0.18934800	4.08727600	2.54654100
C	-0.99299000	3.34113700	2.76258600
O	5.00941600	-0.12900900	-2.13718000
C	6.40676800	0.04597400	-2.16935100
O	0.44693500	3.46082300	-1.93778700
C	1.15254800	4.56364700	-2.47599300
O	-6.91619400	-0.57233500	-1.34236900
C	-7.35130800	0.63530900	-1.96889900
O	-5.90986400	-3.66483200	0.93769800
C	-7.08785700	-3.85563700	0.15458600
O	-4.45933500	2.30430800	-0.96106600
C	-3.49226700	3.35797500	-0.98783300
H	2.31316000	0.74646600	-1.41004000
H	-0.04324300	1.09215400	-1.97756100
H	-2.38445400	0.30640900	-1.88135100
H	-1.33435300	-2.44660700	1.25825800
H	1.02110600	-1.69440900	1.12091800
H	4.20039700	2.01084800	-0.58518800
H	4.68154200	0.98897000	0.79469900
H	4.48810700	2.95389200	2.35981300
H	3.94895700	3.99066200	1.02332800
H	-3.56281900	-2.59872700	0.12300000
H	-3.99861600	-1.42036100	-1.15421300
H	6.41387300	-3.53835000	0.07039200
H	6.25859800	-3.18720800	-1.65869400
H	5.84420800	-4.80524800	-1.04586200
H	3.94241400	-2.90190400	-2.70423500
H	2.49267800	-3.15529700	-1.71871400
H	3.51661600	-4.54312900	-2.15658500
H	3.70229900	-5.11521900	0.36634200
H	2.70616000	-3.69365500	0.75434500
H	4.30699300	-3.87997000	1.49431300
H	5.60036600	3.33452600	1.03785400
H	-5.83909500	-2.72799400	1.17224900
H	-6.34738700	-0.34478100	-0.59152000
H	-4.26200700	1.70668200	-0.22534600
H	-7.04967000	-4.87991300	-0.22576200
H	-7.13816900	-3.15763700	-0.68963200
H	-7.99856800	-3.74493700	0.76099600
H	-8.11845300	1.14550600	-1.36835100

H	-7.79490200	0.35261300	-2.92764700
H	-6.51836100	1.32577300	-2.14109800
H	-2.47165800	2.98515700	-1.12997400
H	-3.52771300	3.96429000	-0.07282800
H	-3.74968500	3.99609400	-1.83674100
H	5.20083800	-1.31736400	0.89147600
H	4.78342100	-0.84856000	-1.45813500
H	5.48737900	-2.30299300	3.08130800
H	4.19083400	-1.08565600	3.04021600
H	5.80041900	-0.65365000	3.65968300
H	6.63444000	0.91218300	-2.80468100
H	6.93285000	-0.82577700	-2.59671900
H	6.82975500	0.23032700	-1.16897300
H	2.80514600	-0.56485200	-0.29523600
H	0.69505200	3.65540300	1.82465100
H	0.85044600	3.21876700	-1.07372700
H	-1.53454500	3.80982500	3.59153000
H	-1.65184700	3.33815300	1.88082700
H	-0.78477600	2.29592400	3.03800200
H	0.70493300	4.80255400	-3.44641700
H	1.08087100	5.45511300	-1.83447600
H	2.21766600	4.33802400	-2.63665800

TABLE 11: Cartesian coordinates (B3LYP/6-31+G(d,p)) of solvated transition state corresponding to deprotonation reaction of monomer **2** by *tert*-butoxide.

C	0.80077600	-0.08001000	-0.37551300
C	-0.03327000	-0.45023600	-1.45779300
C	-1.37906800	-0.73155600	-1.27409000
C	-1.96786200	-0.65760700	0.00360400
C	-1.15229300	-0.26199600	1.08312900
C	0.19547900	0.00779400	0.90255500
C	-3.36869800	-1.00667900	0.20842700
Br	-4.66914400	0.66362700	-0.04980000
C	2.24565100	0.10882700	-0.59193700
S	2.91078300	1.54966700	0.25092200
C	4.68468700	1.32493000	-0.17865700
C	5.47523400	2.59082100	0.13774300
O	2.47771400	2.84324000	-0.51742100
O	3.70169800	-1.96973700	0.15358700
C	3.12195700	-3.27457900	0.10470200
C	4.24265100	-4.29826200	0.36855000
C	2.51257800	-3.52663000	-1.28935100
C	2.03489700	-3.41137600	1.18943900
O	5.22821300	-1.26204500	2.27954900
C	4.43442500	-0.85822600	3.37612200
O	2.06908600	5.12770800	0.99071300
C	0.66951300	5.26250000	1.13430500
O	5.73705800	-1.72208300	-1.71204900
C	6.99168800	-1.80398300	-1.06381400
O	1.69653300	2.83534200	-3.18138400
C	0.38178800	3.35631700	-3.17814700
O	-6.48530100	-2.11145800	0.75487100
C	-7.83532300	-2.29295400	0.33600500
O	-5.54337600	1.40087200	3.28383000
C	-4.66888500	0.53108300	3.98939600
O	-6.46854700	-0.60045700	-2.76597400
C	-5.54992300	-1.48996100	-3.38730900
H	2.49157700	0.20381600	-1.65493500
H	0.39616700	-0.50147800	-2.45413700
H	-1.98966900	-1.01236000	-2.12938700
H	-1.58430300	-0.18667200	2.07856900
H	0.80216300	0.28417400	1.75966200
H	4.73331200	1.06398600	-1.23989800
H	5.02553300	0.47221600	0.41483500
H	5.44728100	2.82729000	1.20685200
H	5.08151900	3.44801400	-0.41448400
H	-3.63906000	-1.29970800	1.21921000
H	-3.79832100	-1.68674000	-0.52185300
H	4.71648000	-4.10481500	1.33681300
H	5.01031000	-4.23022500	-0.40904400
H	3.84720800	-5.32208500	0.37294500
H	3.27537000	-3.39226000	-2.06326300
H	1.69323000	-2.82829700	-1.48742000
H	2.11338700	-4.54594800	-1.36696000
H	1.58755900	-4.41353700	1.17924700
H	1.23581000	-2.68018200	1.03409800
H	2.46645000	-3.24013200	2.18206200
H	6.52212400	2.44254500	-0.14841900
H	-5.32772400	1.34780000	2.34045600
H	-6.22536500	-1.19746200	0.56178300
H	-6.01534300	-0.15343400	-2.03409600
H	-4.98663300	0.53877400	5.03535800
H	-3.62358900	0.86997400	3.94437700
H	-4.72603100	-0.50273700	3.61936700
H	-8.53116500	-1.67994200	0.92642400

H	-8.07884700	-3.34597800	0.50155400
H	-7.96595300	-2.05985800	-0.72871400
H	-5.28717100	-2.33459500	-2.73356200
H	-4.62772000	-0.98153500	-3.70085800
H	-6.04225900	-1.88650400	-4.27917500
H	4.63859400	-1.57432400	1.54320500
H	5.01875800	-1.81837600	-1.03939000
H	3.84511900	-1.68885800	3.79783400
H	3.73861400	-0.04472300	3.11687000
H	5.10569900	-0.49038200	4.15998400
H	7.76650700	-1.59731800	-1.81065500
H	7.18297200	-2.80426900	-0.64276100
H	7.09186100	-1.07383600	-0.24731800
H	2.95479100	-1.00438600	-0.16334800
H	2.24840400	4.32656300	0.44813500
H	2.02980300	2.83610600	-2.25624700
H	0.48164000	6.14023000	1.76278400
H	0.16139000	5.41828700	0.16968400
H	0.21064300	4.38844900	1.62231600
H	0.00229400	3.30882300	-4.20500700
H	-0.29587500	2.77614800	-2.53379500
H	0.34931900	4.40778500	-2.85142800
Frequencies --	-1197.8085	4.5463	6.1600
Frequencies --	11.1923	13.7470	15.8681
Frequencies --	17.1719	18.2905	19.2387

TABLE 12: Cartesian coordinates (B3LYP/6-31+G(d,p)) of solvated products corresponding to deprotonation reaction of monomer **2** by *tert*-butoxide.

C	-0.49809100	-1.24801400	-1.94197300
C	0.81352500	-0.90508900	-1.92687600
C	1.38967800	-0.14842300	-0.82731400
C	0.51342000	0.13314700	0.29969400
C	-0.80267600	-0.20523300	0.28604100
C	-1.40231500	-0.89766100	-0.85142400
C	2.68259600	0.27725100	-0.84615500
C	-2.72921200	-1.22630800	-0.94890500
S	-3.92372300	-0.92918400	0.32168800
O	-4.63769700	-2.29141700	0.58633800
C	-5.14531600	0.04410200	-0.65787100
C	-6.43715900	0.23629200	0.13236300
Br	4.59511400	-1.83417400	0.65391100
O	-0.81667800	3.22491000	-0.49949400
C	-0.20176600	3.87894300	-1.65780200
C	-0.52488800	3.06038900	-2.91314500
C	1.31035600	3.98013300	-1.42620900
C	-0.84672400	5.26539300	-1.71568200
O	-3.68515600	3.12366200	-0.40184700
C	-4.15060100	3.98249100	0.63214600
O	-5.45341900	-3.48311000	-1.76987800
C	-5.03095700	-4.83222200	-1.85085700
O	-5.26062000	-3.05280000	3.19689000
C	-4.17844600	-3.83791300	3.66109000
O	-0.41439200	4.71634300	1.95794700
C	0.27083700	3.94270300	2.93557200
O	7.41089300	-0.15151100	0.15082000
C	8.37361800	-0.92481800	0.84067700
C	5.28944300	-2.64410700	-3.17942500
O	4.05781700	-2.22371100	-2.61706500
C	4.02106000	0.84576700	3.52974100
O	3.10898700	0.49529900	2.50175600
H	-3.12408000	-1.76767900	-1.80568200
H	-0.90814100	-1.81108900	-2.77606200
H	1.47617400	-1.20260000	-2.73544600
H	0.95629100	0.60115400	1.17653500
H	-1.42584400	0.01105300	1.14818600
H	-5.31465300	-0.51474400	-1.58392000
H	-4.64922900	0.99681500	-0.87097700
H	-6.26250800	0.79850900	1.05573300
H	-6.88849200	-0.72519800	0.39083300
H	3.09337100	0.85204400	-0.02437300
H	3.33414200	0.05101500	-1.68270500
H	-0.65372000	5.82031200	-0.79228900
H	-1.92925000	5.18296700	-1.85599600
H	-0.43354600	5.83566200	-2.55386300
H	-1.60766100	2.97385600	-3.04736300
H	-0.10160600	2.05245100	-2.84574200
H	-0.10246600	3.54171900	-3.80197900
H	1.79154600	4.49124000	-2.26735100
H	1.76229800	2.98709100	-1.33577200
H	1.52174800	4.54471500	-0.51300200
H	-7.15188300	0.80026100	-0.47676600
H	3.50029400	-0.25077800	1.99637900
H	6.54172500	-0.59384200	0.25813400
H	4.16637800	-2.19277100	-1.64220200
H	3.61611700	1.72341600	4.04439500
H	5.01249400	1.09987000	3.12922800
H	4.14031100	0.03745800	4.26644000
H	8.15445000	-1.00179600	1.91666300

H	9.34226700	-0.42687300	0.72045500
H	8.45607900	-1.94585000	0.43761900
H	5.53436600	-3.68170600	-2.90615400
H	6.12421400	-1.99831300	-2.87257700
H	5.18776400	-2.59113300	-4.26868700
H	-0.54972400	4.16980100	1.16319500
H	-2.71069900	3.16906200	-0.43486900
H	1.22717900	3.55052700	2.56342900
H	-0.33469000	3.09792500	3.29458700
H	0.47493800	4.60151800	3.78442500
H	-5.23883700	3.87998900	0.67392200
H	-3.90876100	5.03604400	0.43235100
H	-3.73525600	3.71337100	1.61240400
H	-0.49357100	2.30845800	-0.43101600
H	-5.06787300	-2.77500300	2.27636800
H	-5.21453500	-3.12971700	-0.88336900
H	-4.39444100	-4.12017500	4.69698000
H	-4.04852200	-4.76057700	3.07449700
H	-3.22505100	-3.28802300	3.64841400
H	-5.25269400	-5.18990600	-2.86177800
H	-3.94993400	-4.94185800	-1.67625900
H	-5.56207000	-5.47788300	-1.13472200

Experimental set-up of UV-Vis stop flow accessory

To allow very fast and accurate measurements, the UV-Vis spectrophotometer is equipped with a so-called stop flow accessory. The working principle is depicted in Figure S1. Two syringes **1** and **2**, containing a base solution and a monomer solution respectively, are driven forward in such a way that equal amounts of the two solutions meet in the mixing chamber where a static mixer **3** makes a homogeneous solution. This solution is then transferred in the sample cell **4**. When driving forward syringe **1** and **2**, syringe **5** is driven out and it will hit an electric switch **6** which will start the recording of the measurement. With this equipment UV-Vis detection will be started within a few milliseconds.

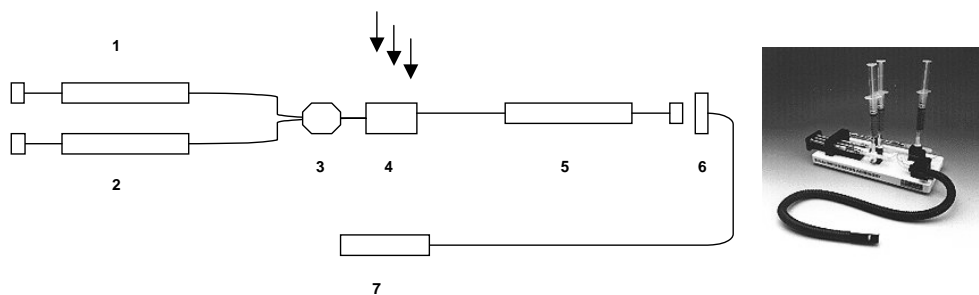


Figure S1. Principle and set-up of the UV-Vis stop flow accessory