Supplementary Information

Why can Dispolreg 007 control the nitroxide mediated polymerization of methacrylates?

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Materials

Toluene (99 %, Fisher Scientific) and d_8-toluene (Sigma Aldrich) were used as received. Methyl methacrylate (MMA, Quimidroga, technical grade) was distilled under reduced pressure and stored at -20 °C before use. The alkoxyamine Dispolreg 007 was synthesized according to the reported procedure.[1]

Instruments and Analysis

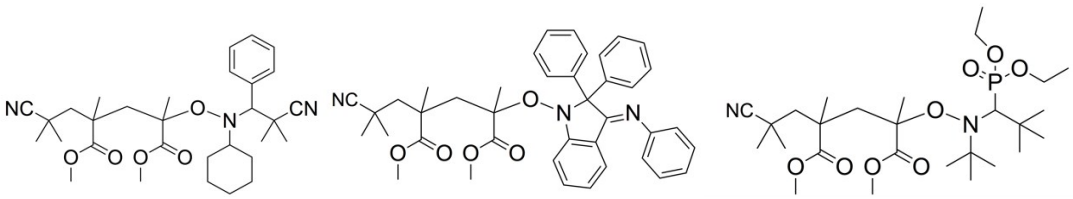
^{1}H NMR spectra were recorded on a Bruker DPX-500 spectrometer using deuterated solvents obtained from Sigma-Aldrich.

SEC traces were obtained on a set up consisting of a pump (LC-20A, Shimadzu), an autosampler (Waters 717), a differential refractometer (Waters 2410) a UV-detector (Waters 2410) and three columns in series (Styragel HR2, HR4 and HR6 with pore sizes ranging from 10^2 to 10^6 Å). Chromatograms were obtained in THF (HPLC grade) at 35 °C using a flow rate of 1 mL.min^{-1}. The equipment was calibrated using narrow polystyrene standards (K = 11.4 10^{-5} dL.g^{-1}, α = 0.716)[2] ranging from 595 to 3.95 × 10^6 Da (5th order universal calibration). The resulting molar mass distributions have been recalibrated using the Mark-Houwink parameters for poly(methyl methacrylate) (K = 9.44 10^{-5} dL.g^{-1}, α = 0.719).[3] All samples were passed through 0.45 μm nylon filter before analysis.

Computational details

All geometry optimizations were carried out in solution within density functional theory (DFT) using the M062X functional[4] combined with the 6-31+G(d,p) basis set.[5] Solvent effects, in anisole, have been estimated using the polarizable continuum model (PCM) approach.[6-8i] To confirm that the optimized structures were minima or transition states on the potential energy surfaces, frequency calculations were carried out at the same level of theory. These frequencies were then used to evaluate the zero-point vibrational energy (ZPVE) and the thermal corrections, at T = 393.15 K, in the harmonic oscillator approximation. Single-point calculations using the 6-311++G(2df,2p) basis set[9] were performed on the optimized structures in order to refine the electronic energy. All the calculations were performed with the Gaussian 09 suite of programs.[ii]

The chemical structures of the three poly(methyl methacrylate) based macro-alkoxyamines are represented in Scheme S1.



Scheme S1: Chemical structures of the poly(methyl methacrylate) based macro-alkoxyamine with (Left) Dispolreg 007, (Middle) DPAIO and (Right) SG1 alkoxyamine/nitroxides.

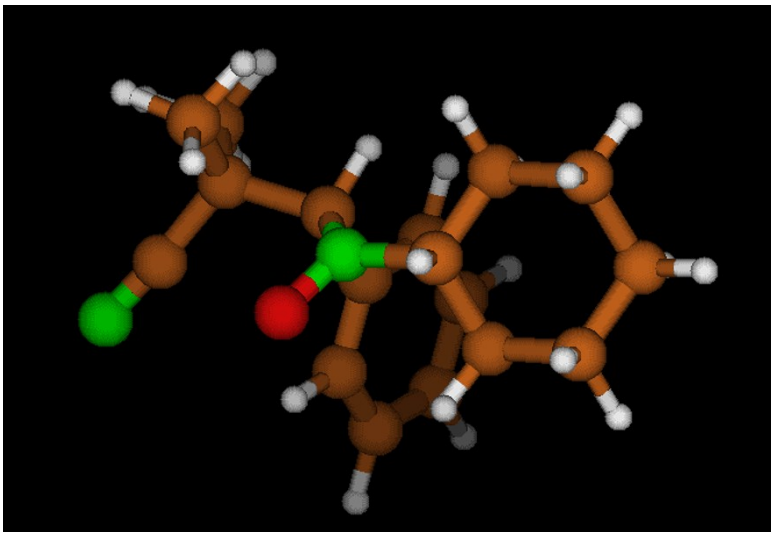


Figure S1. Molecular structure of the most stable conformation of D7, the nitroxide fragment of Dispolreg 007. The dihedral angle between the N-O and the C-H groups is 157.2°, while the one between N-O and C-N groups is 27.6°.

Selected geometrical parameters of the three macro-alkoxyamines studied in this work are collected in Table S1.

Table S1. Selected geometrical parameters for the three macro-alkoxyamines based on poly(methyl methacrylates). Distances in Å, angles (α) and dihedrals (θ) in degrees (°):

	PMMA-D7	PMMA-DPAIO	PMMA-SG1
N-O	1.423	1.396	1.413
O-C	1.439	1.452	1.454
N-$C_1$$^{(a)}$	1.467	1.408	1.477
N-C_2	1.476	1.493	1.500
N··· C	2.879	2.399	2.482
α(N-O-C)	114.7	114.8	119.9
α(O-N- C_1)	107.1	113.2	109.5
θ(O-N-C-H)	164.3	---*	167.9

*In DPAIO there is no α-hydrogen. $^{(a)}C_1$ is the carbon bearing the H_α

The selected geometrical parameters of the three nitroxide fragments are presented in Table S2.

Table S2. Selected geometrical parameters for the three nitroxide fragments. Distances in Å, angles (α) and dihedrals (θ) in degrees (°):

	D7	DPAIO	SG1
N-O	1.276	1.261	1.274
N-$C_1$$^{(a)}$	1.470	1.506	1.466
N-C_2	1.475	1.392	1.497
α(O-N- C_1)	117.8	122.7	117.1
θ(O-N-C_1-H_α)	157.2	---*	173.2

*In DPAIO there is no α-hydrogen. $^{(a)}C_1$ is the carbon bearing the H_α

The Cartesian coordinates of the macro-alkoxyamines based on PMMA and both the alkyl and nitroxide radicals, including the transition states are gathered.

PMMA-D7 (based on Dispolreg 007):

O	0.833742	-0.176160	-0.215727
N	2.066671	0.054562	-0.887295
C	2.915757	-1.117368	-0.645110
H	3.920691	-0.781615	-0.921035
C	2.627211	-2.239592	-1.694152
C	1.247543	-2.755581	-1.585954
N	0.188562	-3.222654	-1.556983
C	2.608281	1.363580	-0.473577
C	2.849432	1.578654	1.022776
C	3.851851	1.733684	-1.285437
H	1.835209	2.080850	-0.790167
C	3.179989	3.053671	1.271245
H	3.692313	0.958322	1.351891
H	1.964783	1.271339	1.587304
C	4.201717	3.207088	-1.041949
H	4.707427	1.118021	-0.975862
H	3.671941	1.541890	-2.349959
C	4.397786	3.491326	0.450943
H	3.358551	3.225873	2.337749
H	2.309248	3.665008	0.993629
H	5.103479	3.473545	-1.602912
H	3.388455	3.836944	-1.428248
H	4.602375	4.556024	0.607038
H	5.281470	2.942059	0.805208
C	3.009776	-1.647592	0.781677
C	1.917050	-2.180863	1.477020
C	4.265137	-1.665104	1.399962
C	2.082040	-2.695905	2.762594
H	0.936014	-2.190431	1.017888
C	4.432955	-2.180214	2.683773
H	5.126664	-1.263902	0.869308
C	3.336050	-2.695856	3.372178
H	1.222907	-3.100447	3.288909
H	5.416790	-2.178938	3.142694
H	3.457829	-3.097630	4.373217
C	-0.314925	0.417550	-0.846527
C	-1.449190	-0.472664	-0.281607
C	-0.213671	0.380814	-2.366075
C	-0.463137	1.843204	-0.278351
C	-2.932765	0.000321	-0.262570
H	-1.163064	-0.701085	0.750691
H	-1.398334	-1.407630	-0.848404
H	-1.123544	0.764241	-2.823297
H	0.628710	0.978116	-2.719456
H	-0.070949	-0.656039	-2.679821
O	-0.316576	2.108684	0.893926
O	-0.802647	2.742770	-1.202248
C	-3.712421	-1.248935	0.230466
C	-3.428092	0.491167	-1.623008
C	-3.074145	1.141408	0.749451
C	-1.021890	4.075740	-0.716987
H	-3.358321	-1.490244	1.238394
H	-3.426414	-2.088042	-0.413955
H	-2.884289	1.384810	-1.933828
H	-3.303087	-0.293768	-2.375367
H	-4.484870	0.764400	-1.583232
O	-3.393714	2.277057	0.467528
O	-2.789041	0.755522	1.995551
H	-1.309201	4.660042	-1.588412
H	-1.818929	4.064931	0.027771
H	-0.100810	4.464577	-0.276981
C	-2.791950	1.794226	2.982244
H	-3.787011	2.238864	3.055509
H	-2.515655	1.311554	3.917294
H	-2.061322	2.557096	2.707696
C	-5.260264	-1.228057	0.302958
C	-5.710052	-2.497033	1.056772
H	-5.357078	-2.438132	2.090232
H	-6.799806	-2.577232	1.062920
H	-5.294049	-3.396017	0.594533
C	-5.834383	0.013373	1.005740
H	-5.388378	0.095725	2.001762
H	-5.633150	0.933251	0.452450
H	-6.916796	-0.087703	1.118340
C	-5.842357	-1.320499	-1.054268
N	-6.329420	-1.427852	-2.098715
C	2.827093	-1.684035	-3.115329
H	3.873432	-1.380859	-3.227154
H	2.607770	-2.452763	-3.860415
H	2.192745	-0.814940	-3.290018
C	3.581071	-3.429130	-1.469983
H	3.452671	-4.165824	-2.266670
H	4.613842	-3.066188	-1.494278
H	3.405968	-3.913701	-0.507713

Alkyl radical:

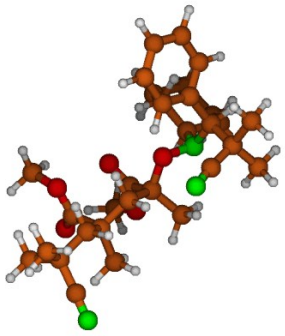
C	-0.949531	0.926865	-1.137236
C	-1.649442	-0.211903	-0.470592
C	-0.691227	0.949978	-2.606388
C	-0.494098	2.026048	-0.299034
C	-3.208466	-0.054206	-0.360417
H	-1.253017	-0.345843	0.541396
H	-1.465712	-1.128143	-1.043136
H	-1.107634	1.853057	-3.067309
H	0.386604	0.970520	-2.810208
H	-1.121424	0.074202	-3.095250
O	-0.630019	2.073753	0.916875
O	0.108326	3.005794	-1.001166

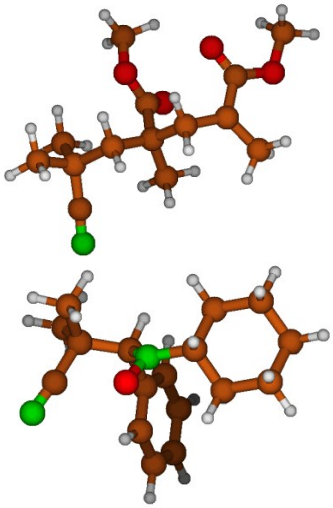
C	-3.720217	-1.336309	0.328570
C	-3.815812	0.161566	-1.747022
C	-3.437532	1.192529	0.492463
C	0.558937	4.124314	-0.233657
H	-3.303426	-1.372468	1.339978
H	-3.307621	-2.194398	-0.215894
H	-3.379544	1.039407	-2.226873
H	-3.636083	-0.716541	-2.375513
H	-4.894496	0.327615	-1.695695
O	-3.709558	2.284263	0.040333
O	-3.251982	0.966166	1.794981
H	1.005602	4.811755	-0.949190
H	-0.283358	4.595213	0.277261
H	1.297153	3.805269	0.504928
C	-3.312928	2.122178	2.638205
H	-4.302901	2.579431	2.574786
H	-3.120387	1.760576	3.646302
H	-2.548503	2.836645	2.329148
C	-5.247515	-1.563528	0.468714
C	-5.466777	-2.766462	1.408995
H	-5.100515	-2.506815	2.406181
H	-6.528683	-3.014354	1.479852
H	-4.924196	-3.646347	1.053413
C	-6.008101	-0.343585	1.015503
H	-5.599222	-0.079089	1.994151
H	-5.929104	0.524830	0.355979
H	-7.067667	-0.584954	1.131692
C	-5.829693	-1.941919	-0.838103
N	-6.307220	-2.276598	-1.837903

Dispolreg 007 radical:

O	-1.048512	-0.808489	-0.407676
N	-0.116031	-0.529987	0.417016
C	-0.077406	0.829017	0.975560
H	0.480212	0.765223	1.915050
C	-1.498598	1.296263	1.397878
C	-2.169966	0.227355	2.277099
H	-3.116221	0.607244	2.669392
H	-2.359154	-0.686569	1.713433
H	-1.511240	-0.002218	3.121091
C	-1.366852	2.616218	2.183309
H	-0.747134	2.449996	3.069892
H	-0.910828	3.400018	1.574704
H	-2.353091	2.954899	2.508180
C	-2.363138	1.575405	0.232682
N	-3.087074	1.870956	-0.620057
C	1.070012	-1.406452	0.401886
C	1.906322	-1.217978	-0.871566
C	1.937385	-1.263156	1.651012
H	0.641172	-2.416975	0.384197
C	3.030627	-2.256793	-0.910122
H	2.336919	-0.208122	-0.876230
H	1.252970	-1.304966	-1.745741
C	3.063883	-2.302945	1.616414
H	2.387053	-0.260788	1.678085
H	1.327125	-1.383405	2.553991
C	3.904748	-2.165697	0.343799
H	3.636983	-2.113821	-1.810170
H	2.593473	-3.262518	-0.976901
H	3.693243	-2.192195	2.504987
H	2.626892	-3.309628	1.658105
H	4.683086	-2.935483	0.322344
H	4.416311	-1.193291	0.354686
C	0.657168	1.784677	0.051244
C	0.336397	1.861105	-1.308442
C	1.686837	2.580770	0.558268
C	1.035200	2.730240	-2.142757
H	-0.447807	1.226845	-1.712130
C	2.386075	3.451753	-0.277190
H	1.947084	2.516579	1.612806
C	2.060148	3.527324	-1.630190
H	0.781384	2.782003	-3.196767
H	3.185144	4.064512	0.127919
H	2.604360	4.201086	-2.284373

The graphical representation is the following: alkoxyamine with PMMA-D7 (Top), alkyl radical (center) and D7, the nitroxide fragment of Dispolreg 007 (Below):





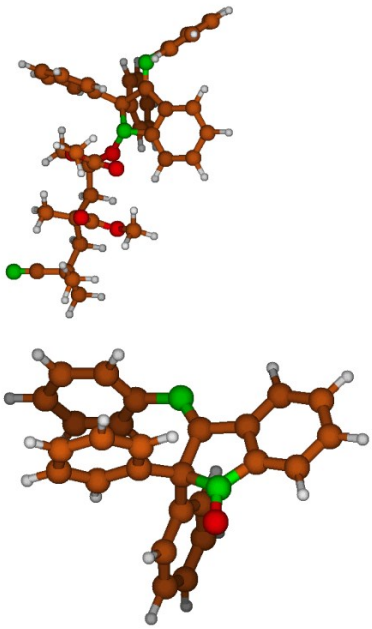
PMMA-DPAIO:

O	-0.382831	0.520428	-0.691075
C	-1.448581	0.666072	0.283923
C	-2.701731	0.474009	-0.607304
C	-1.386735	2.055461	0.907551
C	-1.340473	-0.473225	1.307054
C	-4.083195	0.093685	0.005292
H	-2.445799	-0.296161	-1.340770
H	-2.829811	1.415278	-1.153641
H	-2.311999	2.292810	1.431203
H	-0.564833	2.140455	1.617343
H	-1.241733	2.780550	0.101896
O	-1.192990	-1.633867	0.998962
O	-1.490999	-0.051251	2.558715
C	-5.055795	0.150175	-1.204062
C	-4.521869	1.015272	1.143414
C	-4.000471	-1.339372	0.543096
C	-1.496191	-1.079996	3.560655
H	-4.724271	-0.592616	-1.937500
H	-4.937588	1.133369	-1.674022
H	-3.829235	0.953887	1.984913
H	-4.578817	2.050067	0.791942
H	-5.504445	0.728299	1.524030
O	-4.145902	-1.646199	1.706639
O	-3.735832	-2.227948	-0.418481
H	-1.648191	-0.564009	4.506046
H	-2.309460	-1.779135	3.359115
H	-0.539185	-1.604974	3.554855
C	-3.534751	-3.576943	0.022031
H	-4.441065	-3.953640	0.501144
H	-3.309048	-4.148415	-0.876119
H	-2.699725	-3.607304	0.723965
C	-6.574451	-0.083200	-1.000974
C	-7.217023	-0.212934	-2.397888
H	-6.833862	-1.116474	-2.880592
H	-8.303712	-0.293274	-2.317302
H	-6.974322	0.649744	-3.023849
C	-6.908233	-1.332619	-0.169041
H	-6.426390	-2.202959	-0.625446
H	-6.570661	-1.245189	0.865704
H	-7.988329	-1.499077	-0.162927
C	-7.195746	1.098034	-0.362272
N	-7.716301	2.021639	0.101920
C	1.240444	-1.166592	-0.759795
C	1.990128	0.975357	-0.192748
C	2.629628	-1.308998	-0.645110
C	0.449934	-2.143125	-1.357001
C	3.140958	-0.053957	-0.062459
C	3.258530	-2.469241	-1.102566
C	1.093115	-3.287442	-1.824318
H	-0.622607	-2.013701	-1.434736
C	2.477668	-3.458483	-1.695912
H	4.333207	-2.590184	-1.020084
H	0.503457	-4.066675	-2.297884
H	2.946175	-4.362123	-2.070387
N	0.823204	0.043693	-0.173135
C	1.904829	1.922526	0.994225
C	1.735552	3.299102	0.857929
C	1.896250	1.363457	2.278378
C	1.558371	4.105828	1.984712
H	1.713879	3.751443	-0.127677
C	1.716429	2.162525	3.401228
H	2.009112	0.288187	2.393360
C	1.545876	3.542091	3.256860
H	1.418924	5.175147	1.860580
H	1.704685	1.711591	4.388671
H	1.402257	4.168525	4.131568
C	2.236187	1.657164	-1.548680
C	3.346445	2.506073	-1.662060
C	1.473194	1.395410	-2.688578
C	3.662536	3.109142	-2.874996
H	3.970568	2.684044	-0.790742
C	1.794345	1.998207	-3.907394
H	0.624792	0.724563	-2.639782
C	2.881971	2.860355	-4.005360
H	4.522977	3.767981	-2.938413
H	1.187108	1.785237	-4.781668
H	3.126909	3.328337	-4.953627
N	4.260534	0.274989	0.437106
C	5.284798	-0.693577	0.533498
C	5.243746	-1.666580	1.537985
C	6.372477	-0.643585	-0.343359
C	6.268485	-2.604480	1.638238
H	4.400590	-1.686025	2.222701
C	7.388981	-1.591563	-0.241297
H	6.399570	0.126908	-1.108141
C	7.341295	-2.576683	0.745987
H	6.226132	-3.361866	2.415023
H	8.222977	-1.557605	-0.935646
H	8.136577	-3.310684	0.824290

DPAIO nitroxide:

C	2.908407	2.007827	0.520847
C	3.634883	1.008286	1.172098
C	4.699537	1.343659	2.000993
C	5.005324	2.694200	2.165303
C	4.262752	3.685261	1.502295
C	3.199266	3.362797	0.663634
C	1.803630	-0.050397	-0.034657
C	3.102640	-0.307024	0.778096
H	5.267362	0.566199	2.501613
H	5.826293	2.986488	2.810943
H	4.524287	4.728512	1.647126
H	2.618360	4.114705	0.142682
N	1.915326	1.433363	-0.267719
O	1.102464	2.073182	-0.988249
N	3.697094	-1.395741	1.049693
C	3.228756	-2.654694	0.604440
C	2.182259	-3.322767	1.245207
C	3.903553	-3.273139	-0.455242
C	1.780669	-4.578640	0.789087
H	1.681360	-2.859682	2.088177
C	3.486261	-4.518201	-0.911362
H	4.728944	-2.751827	-0.930612
C	2.419177	-5.176232	-0.295364
H	0.960544	-5.087294	1.286729
H	3.996182	-4.976570	-1.753264
H	2.097806	-6.149661	-0.651401
C	0.540027	-0.238850	0.805617
C	-0.710539	-0.095271	0.192046
C	0.599124	-0.424095	2.189021
C	-1.878098	-0.171098	0.945957
H	-0.765349	0.079832	-0.877567
C	-0.571654	-0.499906	2.944072
H	1.557527	-0.515679	2.692241
C	-1.812717	-0.379149	2.324357
H	-2.840429	-0.064439	0.455545
H	-0.507853	-0.651683	4.016810
H	-2.723916	-0.440542	2.910818
C	1.829786	-0.775949	-1.375001
C	2.733928	-0.344498	-2.350471
C	1.050533	-1.907082	-1.621308
C	2.860382	-1.035825	-3.552172
H	3.344805	0.536932	-2.170903
C	1.176263	-2.598761	-2.824700
H	0.363436	-2.270677	-0.864549
C	2.080746	-2.167458	-3.792560
H	3.565798	-0.688729	-4.300461
H	0.571326	-3.483487	-2.996890
H	2.178886	-2.708349	-4.728542

And the graphical representation is: the macro-alkoxyamine PMMA-DPAIO (Top), and the nitroxide DPAIO (Below).



PMMA-SG1:

O	0.942020	-0.942331	-0.513499
N	2.296512	-0.938259	-0.111418
C	3.008187	0.165019	-0.787495
H	4.070764	-0.029902	-0.604447
C	-0.111677	-0.895077	0.487327
C	-1.145862	0.003723	-0.239381
C	0.331014	-0.359164	1.840944
C	-0.706359	-2.317427	0.556996
C	-2.636526	0.069702	0.204704
H	-1.124666	-0.305288	-1.289702
H	-0.728074	1.012955	-0.188119
H	-0.396029	-0.614532	2.608002
H	1.299472	-0.774533	2.115550
H	0.433306	0.724845	1.789900
O	-0.926454	-2.988151	-0.428009
O	-1.005451	-2.717708	1.793173
C	-3.227544	1.221891	-0.650881
C	-2.808317	0.317360	1.703069
C	-3.311332	-1.256610	-0.156195
C	-1.619662	-4.010849	1.895260
H	-3.128650	0.944403	-1.705823
H	-2.591924	2.101421	-0.493507
H	-2.427408	-0.525992	2.279678

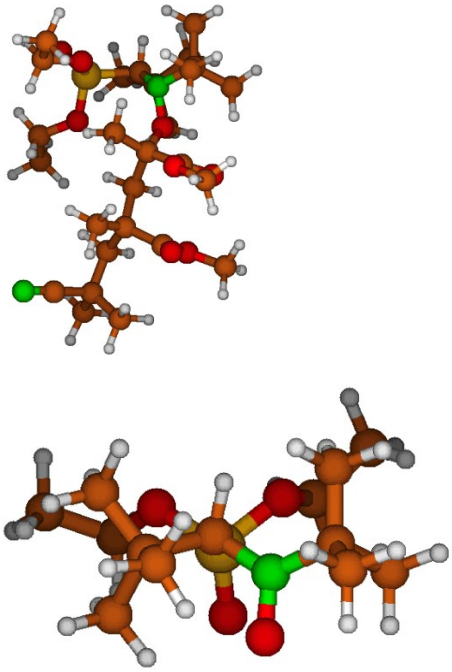
H	-2.278049	1.228904	1.997687
H	-3.861619	0.430885	1.969099
O	-3.758943	-2.044782	0.649731
O	-3.337387	-1.472556	-1.473942
H	-1.801040	-4.163586	2.956932
H	-2.555423	-4.014948	1.334635
H	-0.942057	-4.773116	1.504538
C	-3.843876	-2.748824	-1.882970
H	-4.883897	-2.858459	-1.567590
H	-3.766699	-2.761314	-2.968084
H	-3.234023	-3.539188	-1.441369
C	-4.695633	1.676643	-0.448652
C	-5.055401	2.629779	-1.607484
H	-5.043238	2.066855	-2.545019
H	-6.053167	3.052070	-1.465482
H	-4.334748	3.448792	-1.680415
C	-5.707274	0.519645	-0.406551
H	-5.604589	-0.074859	-1.319500
H	-5.556650	-0.131640	0.457144
H	-6.725391	0.914536	-0.363180
C	-4.817320	2.468385	0.795489
N	-4.931483	3.125411	1.741561
C	2.854832	-2.330504	-0.110830
C	2.474842	-2.976789	1.231063
C	2.306549	-3.204499	-1.247409
C	4.386975	-2.289690	-0.147511
H	2.910437	-2.413112	2.062003
H	1.395205	-3.027972	1.381149
H	2.855630	-4.002384	1.264951
H	2.445920	-2.746913	-2.227116
H	2.829638	-4.166295	-1.241834
H	1.238715	-3.386442	-1.120305
H	4.758109	-3.300288	0.042133
H	4.784700	-1.969873	-1.112314
H	4.782492	-1.637930	0.638876
C	2.888190	0.428074	-2.343676
C	3.863210	-0.489838	-3.100525
C	1.472676	0.239899	-2.906577
C	3.325901	1.865493	-2.687206
H	4.898887	-0.292932	-2.799582
H	3.659797	-1.549524	-2.951729
H	3.785197	-0.289241	-4.174271
H	0.753717	0.871639	-2.376583
H	1.483480	0.532653	-3.962905
H	1.131566	-0.794449	-2.833055
H	3.341685	1.964205	-3.777274
H	2.631034	2.613047	-2.295520
H	4.322175	2.099826	-2.303873
P	2.826064	1.674410	0.258926
O	3.765884	2.813317	0.058698
O	1.284331	2.097379	0.063102
O	2.969094	1.049745	1.734035
C	2.922640	1.939632	2.863283
C	3.237639	1.128204	4.101293
H	1.915439	2.372606	2.929527
H	3.644307	2.748609	2.713151
H	3.204397	1.769389	4.985887
H	2.508842	0.322857	4.225472
H	4.235666	0.689945	4.023675
C	0.797026	3.417251	0.380951
C	0.222552	4.043924	-0.872606
H	1.611103	4.024454	0.787487
H	0.029096	3.287023	1.152255
H	-0.249470	5.000334	-0.631889
H	1.011315	4.219383	-1.608314
H	-0.528890	3.385416	-1.318711

SG1:

N	-1.399552	1.134414	-0.524928
O	-2.610534	1.237454	-0.143004
C	-0.563683	0.101308	0.163969
C	0.878222	0.120006	-0.338169
C	-0.599799	0.426444	1.660919
C	-1.204829	-1.265492	-0.102131
H	0.941801	-0.132501	-1.400254
H	1.356828	1.089091	-0.160550
H	1.440102	-0.632065	0.222461
H	-1.629823	0.439437	2.022396
H	-0.039530	-0.333749	2.212597
H	-0.145988	1.403552	1.854596
H	-0.652390	-2.042124	0.435203
H	-2.241854	-1.265951	0.240915
H	-1.185530	-1.493826	-1.171607
C	-0.990595	1.944677	-1.676065
H	0.089856	1.832745	-1.792011
C	-1.293396	3.466290	-1.496943
C	-2.729958	3.831740	-1.893304
C	-1.050457	3.847552	-0.029474
C	-0.299069	4.258205	-2.362040
H	-2.900503	3.685311	-2.966095
H	-3.453549	3.226319	-1.344077
H	-2.907577	4.890032	-1.674475
H	-0.050664	3.535241	0.295970
H	-1.112404	4.935651	0.073285
H	-1.789884	3.392179	0.633217
H	-0.516950	5.328129	-2.278970
H	0.729036	4.096507	-2.017794
H	-0.358262	3.975932	-3.415106
P	-1.709587	1.133508	-3.169379
O	-3.147162	0.766227	-3.168282
O	-1.290341	2.070192	-4.408139
O	-0.696790	-0.113923	-3.258457
C	-2.238337	2.428990	-5.440706
C	-1.884799	3.810994	-5.946154
H	-3.248851	2.391038	-5.025321
H	-2.161846	1.681837	-6.236234

H	-2.549795	4.080428	-6.770964
H	-1.998068	4.555586	-5.153386
H	-0.853573	3.837722	-6.307575
C	-1.006887	-1.199814	-4.157679
C	0.109160	-2.215384	-4.048591
H	-1.084483	-0.803900	-5.176747
H	-1.973518	-1.623616	-3.870266
H	-0.092788	-3.060965	-4.710895
H	1.064489	-1.767770	-4.333275
H	0.187893	-2.588087	-3.023716

And the graphical representation is: macro-alkoxyamine (Top) and SG1 nitroxide (below):



The cartesian coordinates for the transition states corresponding to the intermolecular disproportionation are:

TS D007:

O	-1.075140	0.113529	-1.326665
N	-2.260217	0.383058	-0.803508
C	-2.952296	-0.778300	-0.238935
H	-2.242714	-1.601679	-0.374583
C	0.993484	-0.654088	-1.388620
C	1.783066	0.403579	-0.682598
C	0.689533	-0.599319	-2.766202
C	0.572007	-1.818509	-0.573485
C	3.332496	0.165284	-0.646469
H	1.425263	0.491815	0.347911
H	1.616133	1.360593	-1.191363
H	0.501553	-1.540856	-3.277621
H	-0.493832	-0.156192	-2.548293
H	1.208934	0.156772	-3.351860
O	0.767115	-1.920546	0.625855
O	-0.067817	-2.759695	-1.284861
C	3.908970	1.298705	0.223217
C	3.905035	0.142628	-2.065326
C	3.539591	-1.209167	-0.010248
C	-0.488129	-3.910483	-0.547628
H	3.459400	1.216532	1.215990
H	3.571442	2.252538	-0.200865
H	3.431400	-0.641782	-2.656993
H	3.733435	1.108762	-2.551958
H	4.978400	-0.064775	-2.056939
O	3.571511	-2.242114	-0.643772
O	3.617193	-1.159287	1.320738
H	-0.959448	-4.569571	-1.274216
H	0.372328	-4.397821	-0.085251
H	-1.202002	-3.627889	0.231728
C	3.724127	-2.427946	1.975770
H	4.631790	-2.938065	1.646405
H	3.771151	-2.206427	3.040102
H	2.845870	-3.032351	1.741870
C	5.450317	1.419587	0.397504
C	5.743511	2.022563	1.784668
C	6.081538	2.318033	-0.685085
H	5.233871	2.987717	1.862750
H	5.375496	1.367407	2.578161
H	6.816026	2.181518	1.922482
H	7.162578	2.389930	-0.540932
H	5.888967	1.945562	-1.692125
H	5.652639	3.320547	-0.596846
C	6.115002	0.100999	0.337144
N	6.670725	-0.913164	0.285087
C	-2.456051	1.751121	-0.327733
C	-1.424438	2.165033	0.731384
C	-2.438702	2.716486	-1.516385
H	-3.457929	1.777374	0.118670
C	-1.660651	3.607578	1.187173
H	-0.427104	2.072574	0.281162
H	-1.467634	1.476391	1.582122
C	-2.666767	4.158972	-1.057803
H	-1.463668	2.632489	-2.015593
H	-3.206294	2.409797	-2.235828
C	-1.642378	4.574454	0.000887
H	-0.905798	3.893218	1.927673
H	-2.636184	3.670532	1.689996
H	-2.624925	4.834578	-1.918691
H	-3.677631	4.246450	-0.635612

H	-1.839221	5.597302	0.339709
H	-0.639092	4.573142	-0.448496
C	-3.204804	-0.654008	1.257320
C	-2.209899	-1.124709	2.121681
C	-4.339064	-0.046106	1.806158
C	-2.339684	-0.988801	3.502378
H	-1.309807	-1.576813	1.708475
C	-4.469541	0.093169	3.187931
H	-5.131556	0.329112	1.165292
C	-3.471018	-0.376136	4.040231
H	-1.555053	-1.358453	4.155157
H	-5.355337	0.569546	3.596269
H	-3.575175	-0.266267	5.115054
C	-4.166454	-1.175972	-1.133169
C	-3.635791	-1.510101	-2.541134
C	-4.910978	-2.385863	-0.548690
H	-2.954773	-2.364308	-2.469307
H	-4.460332	-1.771289	-3.208798
H	-3.089553	-0.662035	-2.960621
H	-5.685300	-2.724216	-1.241348
H	-4.193678	-3.200790	-0.405451
H	-5.371708	-2.158445	0.413913
C	-5.093838	-0.035054	-1.277162
N	-5.819510	0.855954	-1.417624

TS DPAIO:

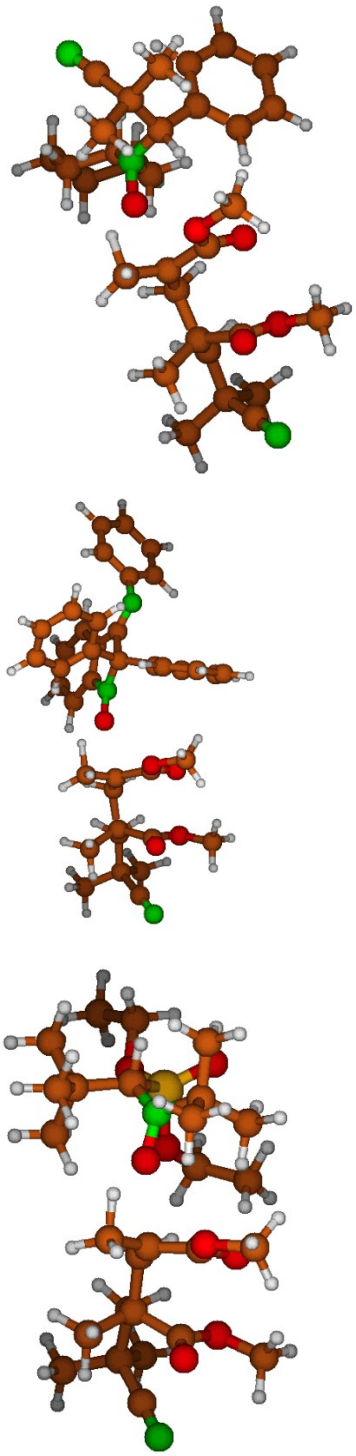
O	0.007008	-0.408350	1.014387
C	-2.200038	-0.854668	0.949735
C	-2.790669	0.484291	0.646885
C	-1.884725	-1.260469	2.262695
C	-2.003553	-1.763784	-0.217391
C	-4.359731	0.508530	0.595578
H	-2.402953	0.839142	-0.312133
H	-2.491820	1.184561	1.434342
H	-1.800331	-2.328609	2.448140
H	-0.698492	-0.876647	2.167641
H	-2.316007	-0.670700	3.069906
O	-2.166268	-1.408468	-1.368739
O	-1.665582	-3.002328	0.138124
C	-4.739589	1.924913	0.123635
C	-4.941725	0.154338	1.966469
C	-4.779753	-0.565323	-0.409845
C	-1.526073	-3.927066	-0.946704
H	-4.302033	2.073177	-0.866629
H	-4.257658	2.644752	0.796552
H	-4.613673	-0.837276	2.281078
H	-4.617969	0.890313	2.710282
H	-6.034173	0.135581	1.939687
O	-4.951264	-1.726951	-0.107914
O	-4.873523	-0.105186	-1.656273
H	-1.154350	-4.848373	-0.502478
H	-2.499350	-4.089231	-1.416127
H	-0.818910	-3.539307	-1.680711
C	-5.186887	-1.087159	-2.651547
H	-6.160210	-1.532268	-2.434934
H	-5.209873	-0.549581	-3.597130
H	-4.412502	-1.856276	-2.658930
C	-6.241689	2.327001	0.056489
C	-6.429466	3.337070	-1.091692
C	-6.722074	2.966776	1.374682
H	-5.770853	4.193374	-0.917202
H	-6.168965	2.885125	-2.051976
H	-7.461905	3.693074	-1.133432
H	-7.777795	3.240931	1.305337
H	-6.591773	2.298473	2.227150
H	-6.138879	3.875117	1.551812
C	-7.111569	1.165783	-0.225053
N	-7.824214	0.276978	-0.430475
C	1.435997	1.453049	0.736343
C	2.325367	-0.678799	0.269844
C	2.745346	1.717833	0.286531
C	0.604618	2.461259	1.229183
C	3.311848	0.434719	-0.171512
C	3.236241	3.024639	0.317812
C	1.120149	3.753311	1.260394
H	-0.398132	2.230380	1.568546
C	2.417279	4.040117	0.811358
H	4.239754	3.251459	-0.024549
H	0.500909	4.559623	1.642010
H	2.787421	5.058539	0.849146
C	2.022522	-1.661203	-0.857302
C	2.104464	-3.045051	-0.708543
C	1.649947	-1.134991	-2.100172
C	1.874704	-3.887183	-1.799656
H	2.357896	-3.477559	0.253057
C	1.404135	-1.971844	-3.182976
H	1.559453	-0.057580	-2.220124
C	1.535028	-3.355176	-3.039822
H	1.955052	-4.962271	-1.670473
H	1.119327	-1.546003	-4.139789
H	1.359178	-4.010625	-3.887170
C	2.929737	-1.300028	1.537637
C	4.110907	-2.047761	1.440958
C	2.378259	-1.067136	2.798459
C	4.707144	-2.577830	2.580841
H	4.566318	-2.201920	0.467163
C	2.979124	-1.597901	3.942324
H	1.479990	-0.467775	2.898873
C	4.139849	-2.358229	3.837893
H	5.619975	-3.158004	2.488002
H	2.535662	-1.409608	4.915063
H	4.605446	-2.771298	4.727141
N	4.373507	0.137570	-0.802084
C	5.286265	1.159807	-1.142767
C	6.355775	1.449948	-0.289616
C	5.154475	1.845041	-2.354626

C	7.262924	2.450684	-0.631690
H	6.453178	0.899350	0.641645
C	6.066810	2.843913	-2.688271
H	4.328472	1.597956	-3.015216
C	7.120605	3.155413	-1.828002
H	8.083913	2.680528	0.040626
H	5.952436	3.381081	-3.624878
H	7.828920	3.934130	-2.091071
N	1.135058	0.121666	0.594520

TS SG1:

O	1.351848	-1.274331	0.866283
N	2.576784	-1.214930	0.434052
C	3.261347	0.067300	0.535237
H	4.316184	-0.129906	0.320643
C	-0.983907	-1.348554	0.978460
C	-1.447917	0.025406	0.615212
C	-0.564552	-1.712458	2.286125
C	-1.046550	-2.364684	-0.086631
C	-2.987652	0.284214	0.778005
H	-1.182322	0.225227	-0.424803
H	-0.931324	0.759458	1.243344
H	-0.717721	-2.750811	2.577441
H	0.648637	-1.658840	2.077917
H	-0.776264	-0.987309	3.072005
O	-1.390876	-2.138669	-1.237262
O	-0.689830	-3.591903	0.330037
C	-3.221657	1.713179	0.250403
C	-3.416197	0.100470	2.234323
C	-3.694456	-0.762790	-0.081530
C	-0.757820	-4.625501	-0.654352
H	-2.910828	1.731871	-0.797734
H	-2.549307	2.388339	0.794803
H	-3.172357	-0.904567	2.581364
H	-2.901967	0.830359	2.869094
H	-4.496119	0.226948	2.350035
O	-4.055709	-1.842040	0.334562
O	-3.820310	-0.385078	-1.356419
H	-0.448158	-5.536491	-0.145006
H	-1.779122	-4.722367	-1.028527
H	-0.085302	-4.404910	-1.486334
C	-4.387595	-1.364635	-2.232530
H	-5.395927	-1.618888	-1.899119
H	-4.412955	-0.899981	-3.216378
H	-3.755961	-2.254736	-2.239029
C	-4.640658	2.343014	0.341441
C	-4.810796	3.339224	-0.821629
C	-4.858753	3.086033	1.674723
H	-4.013783	4.086864	-0.762618
H	-4.740080	2.827329	-1.784640
H	-5.774690	3.850706	-0.760370
H	-5.859107	3.525305	1.708205
H	-4.738749	2.429101	2.537004
H	-4.123385	3.892751	1.746575
C	-5.700606	1.321593	0.210949
N	-6.556424	0.547347	0.121048
C	3.030512	-2.388540	-0.355979
C	2.210663	-2.455103	-1.654222
C	4.518559	-2.283530	-0.684485
C	2.774914	-3.631883	0.504018
H	1.141772	-2.401725	-1.429291
H	2.472070	-1.620515	-2.310380
H	2.416419	-3.395425	-2.176787
H	5.126981	-2.208560	0.223550
H	4.815390	-3.194773	-1.210846
H	4.726633	-1.434538	-1.342248
H	3.083659	-4.525602	-0.046436
H	3.351328	-3.577007	1.433801
H	1.713686	-3.718828	0.749601
C	3.217657	0.682292	1.969576
C	4.367851	1.692260	2.113054
C	1.895337	1.391414	2.288327
C	3.461909	-0.455934	2.972381
H	5.334621	1.233038	1.875901
H	4.223561	2.564812	1.472559
H	4.410703	2.044915	3.148567
H	1.051914	0.706047	2.195012
H	1.930208	1.773290	3.314710
H	1.730368	2.240069	1.616593
H	3.551984	-0.038621	3.980480
H	2.643523	-1.180448	2.971291
H	4.392541	-0.987425	2.740764
P	2.761257	1.118926	-0.900118
O	3.369773	0.649718	-2.176717
O	1.169301	1.118308	-0.829667
O	3.107992	2.666674	-0.596979
C	4.336763	3.227880	-1.110412
C	4.360350	4.692870	-0.734567
H	4.361630	3.082299	-2.192880
H	5.186720	2.692680	-0.670216
H	5.275929	5.156006	-1.111185
H	3.502175	5.211462	-1.169028
H	4.329257	4.815403	0.351413
C	0.431035	1.656883	-1.954475
C	0.083331	0.554935	-2.934389
H	1.015584	2.453503	-2.427436
H	-0.461822	2.109437	-1.515192
H	-0.554024	0.957010	-3.727903
H	0.993521	0.150703	-3.384281
H	-0.451283	-0.257012	-2.430827

And the graphical representation is: D007 (Top), DPAIO (center) and SG1 (Below):



Accuracy of the DFT model

As different levels of theory could over- or under-estimate all parameters (geometry, BDE, etc.), the accuracy of the DFT model was checked by a) comparison with other levels of theory, b) comparison with the geometries of known nitroxides, and c) comparison with the bond dissociation energies of known alkoxyamines.

a) Different levels of theory

Although DFT calculations are commonly used for this type of problems (this level of theory has been successfully used to study the homolysis of alkoxyamines),[10, 11] we have tried other levels of theory. G3(MP2)-RAD has reasonable computational cost and it is applicable to chemical systems with up to 100 electrons, approximately. It has been utilised by Coote and coworkers for the calculations of the bond dissociation energies of model alkoxyamines such as $(CH_3)_3$C-TEMPO (120 electrons).[12] However, our system is larger (PMMA-D7 has 292 electrons) and the G3(MP2)-RAD crashed due to the impossibility to allocate the memory needed. The reason is the highly demanding CCSD(T) step, which is only efficiently implemented and practical for systems with up to 20 atoms or 300 basis functions (F. Jensen "Introduction to Computational Chemistry"). We also tried CBS-QB3 that after more than 1100 hours in 32 processors did not finish.

We have then used the CBS-4M methodology to calculate the bond dissociation energies of Dispolreg007 and SG1, that were the extreme values in the DFT calculations.[13] CBS-4M makes use of MP4 calculations instead of CCSD(T), and smaller basis.[14]

The calculated bond dissociation energies (in kcal/mol, gas phase) of the PMMA-alkoxyamines are compared in Table S3.

Table S3. Bond dissociation energies (in kcal.mol^{-1}) of two macro alkoxyamines based on PMMA woth two level of quantum calculations.

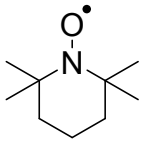
	M062X	CBS-4M
PMMA-D7	38.03	42.93
PMMA-SG1	23.79	30.24

It can be seen that in spite of the higher values provided by CBS-4M, these results confirm that the C-O bond of PMMA-SG1 is more labile than that of PMMA-Dispolreg007.

b) Geometries

In order to validate the geometries obtained by our theoretical level, we utilised the experimental molecular structure of TEMPO, obtained by X-ray diffraction.[15] The results are gathered in Table S4.

Table S4. Comparison of experimental and theoretical values of bond length (in Å) and angles (in degrees) for the TEMPO nitroxide. The experimental data was obtained by X-ray diffraction and the theoretical is obtained through DFT calculations.

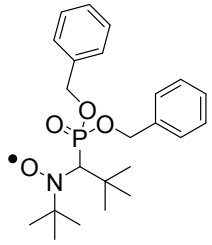
	**Experimental** *(a)*	**Theoretical** *(b)*	ε_{abs} *(c)*
N-O	1.283	1.276	0.007
C_1-C_2	1.508	1.524	0.016
C_2-C_3	1.520	1.534	0.014
C_3-C_4	1.543	1.537	0.006
C_3-C_5	1.513	1.530	0.017
C_3-N	1.488	1.494	0.006
C_3-N-O	116.7	115.8	0.9
C_3-(NO)-C_6	123.6	124.0	0.4
C_1-C_2-C_3	113.5	113.3	0.2
C_2-C_3-N	110.6	109.8	0.8

(a) Extracted from reference 15. *(b)* Calculations carried out with the M062X functional combined with the 6-31+G(d,p) basis set. *(c)* Absolute difference between theoretical and experimental values.

It can be observed in Table S4 that the mean error for the bond lengths is 0.011 Å, while it is of 0.6° for the angles, thus showing that the calculation are in good agreement with the experimental data.

The same comparison can be done with the experimental data of a modified SG1-based nitroxide, in which the -OEt groups have been replaced by -OBz groups.[16] The results are in Table S5.

Table S5. Comparison of experimental and theoretical values of bond length (in Å) and angles (in degrees) for a modified SG1 nitroxide. The experimental data was obtained by X-ray diffraction and the theoretical is obtained through DFT calculations.

	**Experimental** *(a)*	**Theoretical** *(b)*	ε_{abs} *(c)*
N-O	1.278	1.274	0.004
N-C_1	1.479	1.466	0.013
N-C_2	1.491	1.497	0.006
P-O_1	1.455	1.484	0.029
P-O_2	1.574	1.609	0.030
P-O_3	1.583	1.609	0.026
O-N-C_1	116.0	117.1	1.1
O-N-C_2	116.6	116.7	0.1
O_1-P-O_2	114.9	113.4	1.5
O_1-P-O_3	114.7	114.7	0

(a) Extracted from reference 16. *(b)* Calculations carried out with the M062X functional combined with the 6-31+G(d,p) basis set. *(c)* Absolute difference between theoretical and experimental values.

As it can be observed, the largest errors correspond to the phosphor-oxygen bonds, which can be ascribed to the presence of phenyl rings in the experimental structure, increasing the mean error up to 0.018 Å. Regarding the angles, a mean error of 0.7° is obtained, further demonstrating that the calculations are in good agreement with the experimental data.

c) Bond dissociation energies

Regarding the bond dissociation energies, we have used some experimental values from the literature, wherein the BDE (kcal/mol) of several TEMPO-based alkoxyamines is provided.[10]

Table S6. Comparison of experimental and theoretical values of bond dissociation energies (BDE, in kcal/mol) for TEMPO based alkoxyamines with various alkyl fragments.

Alkyl fragment	Experimental BDE[(a)] (kcal/mol)	DFT BDE [(b)] (kcal/mol)	ε_{abs} [(c)]
methyl	47.08	47.90	0.82
benzyl	34.66	35.16	0.50
styryl	30.83	36.13	5.30
cumyl	26.29	29.77	3.48

[(a)] Extracted from reference 10 and references therein. [(b)] Calculations carried out with the M062X functional combined with the 6-31+G(d,p) basis set. [(c)] Absolute difference between theoretical and experimental values.

The calculated values of BDE for all alkoxyamines are above the experimental data. Nevertheless, the mean error is 2.5 kcal/mol (≈ 10.5 kJ/mol), which is also reasonable for the estimation of the BDE.

Table S7. Bond dissociation energy (BDE) and enthalpy differences (ΔH) for the intermolecular disproportionation reaction, in kJ/mol. ΔH^{TS} and ΔH^{react} corresponds to the transition state and reaction enthalpies, respectively.

	BDE	ΔH^{TS}	ΔH^{reac}
Dispolreg 007	142.30	85.74	-81.98
DPAIO	140.61	77.29	-86.72
SG1	84.87	76.56	-90.68

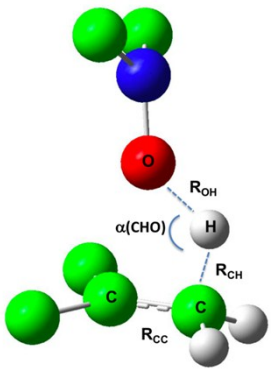


Figure S2. Simplified molecular structure of the transition state in the intermolecular disproportionation reaction

Polymerization model

In order to predict the evolution of monomer conversion and percentage of macromonomers formed during polymerization, a mathematical model was applied, using the following reaction scheme (Scheme S1). This was incorporated into a differential mass balances model, coded in MATLAB.

Alkoxyamine Decomposition / Recombination

$$RN \overset{k_{DA}}{\rightarrow} R^{\bullet} + N^{\bullet} \quad (1)$$

$$R^{\bullet} + N^{\bullet} \overset{k_{CA}}{\rightarrow} RN \quad (2)$$

Alkoxyamine Initiation / Termination

$$R^{\bullet} + R^{\bullet} \overset{k_{TCA}}{\rightarrow} Dead \quad (3)$$

$$R^{\bullet} + R^{\bullet} \overset{k_{TDA}}{\rightarrow} R^{=} + RH \quad (4)$$

$$R^{\bullet} + M \overset{k_{ini}}{\rightarrow} P^{\bullet} \quad (5)$$

Inhibition

$$R^{\bullet} + Inh \overset{k_{inh}}{\rightarrow} Dead \quad (6)$$

Propagation

$$P_n^{\bullet} + M \overset{k_p}{\rightarrow} P_{n+1}^{\bullet} \quad (7)$$

Macroalkoxyamine Recombination / Decomposition

$$P^{\bullet} + N^{\bullet} \overset{k_C}{\rightarrow} PN \quad (8)$$

$$PN \overset{k_D}{\rightarrow} P^{\bullet} + N^{\bullet} \quad (9)$$

Termination / Inhibition

$$P^{\bullet} + P^{\bullet} \overset{k_{TC}}{\rightarrow} Dead \quad (10)$$

$$P^{\bullet} + P^{\bullet} \overset{k_{TD}}{\rightarrow} P^{=} + PH \quad (11)$$

$$P^{\bullet} + Inh \overset{k_{inh}}{\rightarrow} Dead \quad (12)$$

Transfer to monomer

$$P^{\bullet} + M \overset{k_{TM}}{\rightarrow} R^{\bullet} + PH \quad (13)$$

Disproportionation by Nitroxide

$$P^{\bullet} + N^{\bullet} \overset{k_{TNC}}{\rightarrow} P_{Disp}^{=} + NH \quad (14)$$

$$PN \overset{k_{TND}}{\rightarrow} P_{Disp}^{=} + NH \quad (15)$$

Scheme S2. Nitroxide mediated polymerization of methacrylates.

Table S8. Estimated rate constants

Reactions	Rate constants	Value (s^{-1} and $M^{-1}.s^{-1}$)	References
(1)	k_{DA}	$k_{DA} = 1.1\times10^{13}\ e^{(-112000/RT)}$ *(a)*	[1]
(2)	k_{CA}	3.1×10^{6}	This work
(3)	k_{TCA}	$k_t^{1,1}\times1.7$	[17] at 100 °C
		$k_t^{1,1} = 2.33\times10^{10}\ e^{(-9000/RT)}$	[18, 19]
(4)	k_{TDA}	$k_{TCA}/2.7$	[17] at 100 °C
(5)	k_{ini}	$16.8\times k_p$	[20, 21] at 60 °C
(6), (12)	k_{inh}	$6\times k_{inh0}$	This work
		$k_{inh0} = 33000 * k_p$	[22] at 60 °C
(7)	k_p	$2.673\times10^{6}\ e^{(-22360/RT)}$	[23]
(8)	k_C	3.7×10^{5}	This work
(9)	k_D	$k_D = 6.6\times10^{13}\ e^{(-109000/RT)}$	[1]
(10)	k_{TC}	$k_t^{i,i}\times1.7$ *(b)*	[17] at 100 °C
		$k_t^{i,i} = k_t^{1,1}\times i^{-\alpha S}$ for $i \leq 100$	[18]
		$k_t^{i,i} = k_t^{1,1}\times 100^{-\alpha S+\alpha L} \times i^{-\alpha L}$ for $i > 100$	[24]
		with $\alpha_S = 0.63$, $\alpha_L = 0.16$	
		and	
		$k_t^{1,1} = 2.33\times10^{10}\ e^{(-9000/RT)}$	[19]
		for $i > 1000$,	
		$k_t^{i,i} = 1.984\times10^{8}\ e^{(-5890/RT)}$	[23]
(11)	k_{TD}	$k_{TC}/2.7$	[17] at 100 °C
(13)	k_{TM}	$k_p\times7.413\times10^{-2}\ e^{(-23740/RT)}$	[23]
(14)	k_{TNC}	8.3×10^{2}	This work
(15)	k_{TND}	0	This work and [25, 26]

(a) R = 8.314 $J.mol^{-1}.K^{-1}$ with T the temperature in Kelvins.
(b) $k_t^{i,i}$ describes the rate constant for termination of two radicals of length i.

Polymerizations at 90 °C

Online NMR at 90 °C

Dispolreg 007 (8.5 mg, 0.025 mmol, 1equiv), MMA (500 mg, 200 equiv, [M] = 4.35 mol.L^{-1}) and d_8-toluene (500 mg) were added to a vial fitted with a stirring bar and a septum. The solution was deoxygenated with N_2 for 15 minutes. In the mean time, an NMR tube fitted with a Young's tap was deoxygenated with N_2 for 30 minutes. The deoxygenated solution was then added to the NMR tube via a deoxygenated syringe. The NMR tube was placed in a pre-heated NMR machine at 90 °C, and scans were taken every 10 minutes for 900 minutes.

Polymerization at 90 °C

Dispolreg 007 (169 mg, 0.50 mmol, 1equiv), MMA (10 g, 200 equiv, $[M]_0$ = 4.35 mol.L^{-1}) and toluene (10 g) were added to 50 mL round-bottom flask (RBF) fitted with a stirring bar, a thermometer and a septum. The solution was deoxygenated with purging N_2 for 15 minutes. The RBF was placed in a pre-heated oil bath at 96 °C (to reach an internal temperature of *c.a.* 90 °C) and the mixture was left to polymerize for 720 minutes. Samples were taken via a deoxygenated syringe to monitor the evolution of monomer conversion (by ^{1}H NMR), percentage of macromonomers (by ^{1}H NMR) and molar mass (by SEC).

The percentage of macromonomers was calculated as %*MM* = 100 × (3/2) × (***H***$_2$C=C / C***H***$_3$) with ***H***$_2$C=C the integral of the macromonomer vinyl protons at δ = 6.04 and 5.38 ppm and C***H***$_3$ the integral of the polymeric C***H***$_3$ (c,c' in Figures S3-S4, δ = 1.00 ppm)

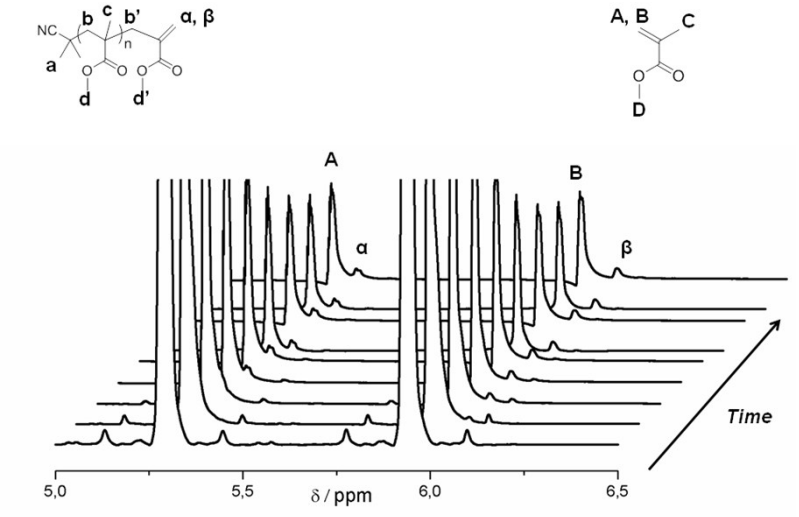


Figure S3. In situ ^{1}H NMR (500 MHz, Toluene-d_8) of the polymerization of methyl methacrylate in the presence of Dispolreg 007 ($[M]_0$ / $[Alkoxyamine]_0$ = 200, $[M]_0$ = 4.35 mol.L^{-1}) at 90 °C.

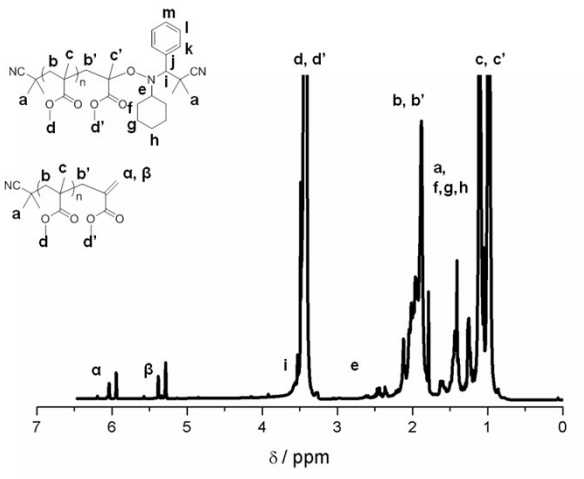


Figure S4. ^{1}H NMR (500 MHz, Toluene-d_8) of the polymerization of methyl methacrylate in the presence of Dispolreg 007 ($[M]_0$ / $[Alkoxyamine]_0$ = 50, $[M]_0$ = 4.35 mol.L^{-1}) at 90 °C after 800 minutes.

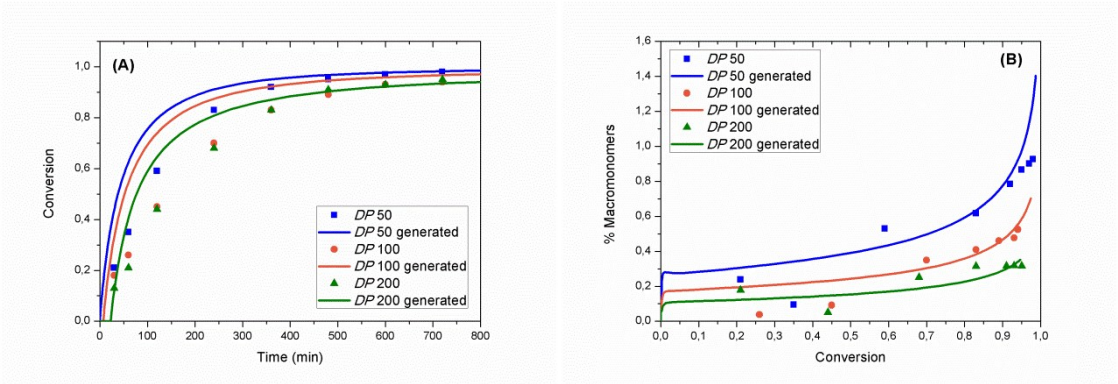


Figure S5. (A) Experimental (Squares, DP_{50}; Up Triangles, DP_{100}; Circles, DP_{200}; obtained from offline NMR measurements) and modeled (lines) evolution of monomer conversion as a function of time. (B) Experimental (Squares, DP_{50}; Up triangles, DP_{100}; Circles, DP_{200}; obtained from offline NMR measurements) and modeled (lines) evolution of percentage of macromonomers %MM = 100 × (3/2) × ($\boldsymbol{H}_2$C=C / C$\boldsymbol{H}_3$) as a function of monomer conversion.

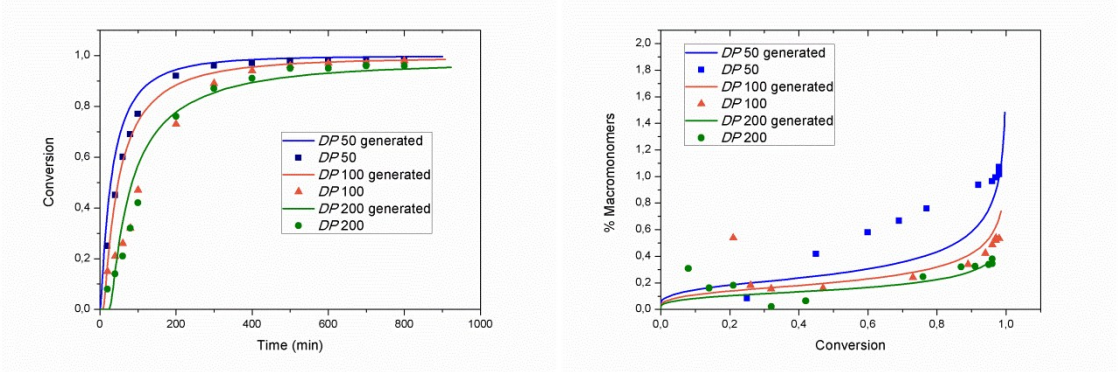


Figure S6. (Left) Experimental (Squares, DP_{50}; Up Triangles, DP_{100}; Circles, DP_{200}) and modeled (lines) evolution of monomer conversion as a function of time using a singular k_t =

6.07×10^7 $M^{-1}s^{-1}$. (Right) Experimental (Squares, DP_{50}; Up triangles, DP_{100}; Circles, DP_{200}) and modeled (lines) evolution of percentage of macromonomers $\%MM = 100 \times (3/2) \times (\boldsymbol{H}_2C{=}C\ /\ C\boldsymbol{H}_3)$ as a function of monomer conversion.

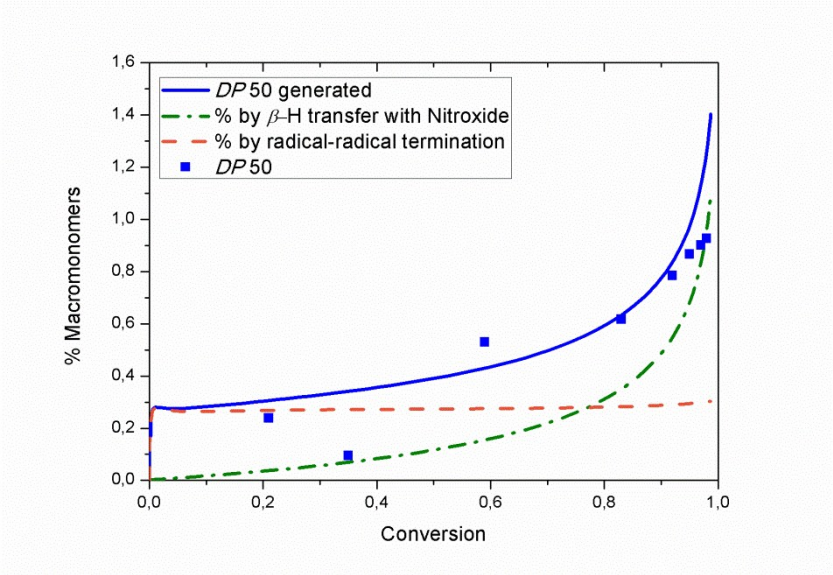


Figure S7. Experimental (Squares, DP_{50}; obtained by offline NMR measurements) and modeled (Total line; by β-H transfer to nitroxide; Dash line, by radical-radical termination by disproportionation i.e. reaction 11 in Scheme S1); Dash-dot line, evolution of percentage of macromonomers $\%MM = 100 \times (3/2) \times (\boldsymbol{H}_2C{=}C\ /\ C\boldsymbol{H}_3)$ as a function of monomer conversion).

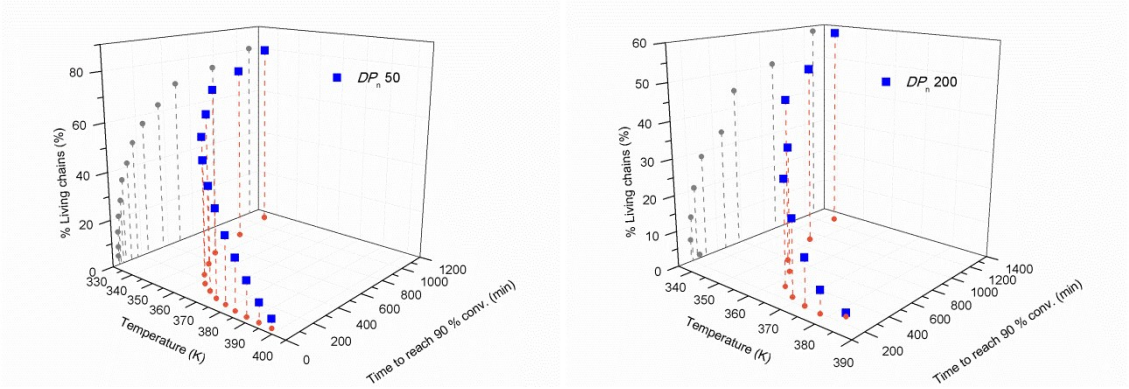


Figure S8. Percentage of "living" chains at 90 % conversion, as a function of time and temperature during the polymerization of MMA in the presence of Dispolreg 007 ($[M]_0 = 4.35$ $mol.L^{-1}$, in the absence of inhibitor). (Left) $DP_n = 50$. (Right) $DP_n = 200$.

Maximum conversion $\boldsymbol{C}_{max)}$

The maximum conversion $\boldsymbol{C}_{max}$, as introduced by Souaille and Fischer is defined as follows,[27]

$$C_{max} = 1 - exp\left(-\frac{3}{2} k_p \left(\frac{[I]_0}{3k_t(k_C + k_{TNC}) k_D f_D^2} \right)^{\frac{1}{3}} F(\infty) \right) \text{, with } F(\infty) = 2^{2/3} \frac{\Gamma(2/3)^2}{3\Gamma(1/3)} \approx 1.08$$

The values of k_p, $k_t^{1,1}$, k_C and k_{TNC} are taken from Table S4. The values of k_t are calculated for each targeted DP_n. For DP_{50}, $k_t^{i,i}$ is calculated as $k_t^{i,i} = k_t^{1,1} \times 50^{-0.63}$ $M^{-1}s^{-1}$. For DP_{100}, $k_t^{i,i}$ is calculated as $k_t^{i,i} = k_t^{1,1} \times 100^{-0.63}$ $M^{-1}s^{-1}$. For DP_{200}, $k_t^{i,i}$ is calculated as $k_t^{i,i} = k_t^{1,1} \times 100^{-0.63+0.16} \times 200^{-0.16}$ $M^{-1}s^{-1}$. $F(\infty)$ is calculated using the Gamma function. The values of $\boldsymbol{C}_{max}$ for DPAIO are calculated assuming C-O bond breakage only, using the rate constants from literature.[28]

k_D values reported in literature

The values of the bond dissociation energies calculated in this work (Table 1) differ from the activation energies the activation energies of the macroalkoxyamines PMMA-D7 (109 kJ.mol^{-1}),[1] PMMA-SG1 (≈ 100 kJ.mol^{-1})[29] and PMMA-DPAIO (126 kJ.mol^{-1})[28]. However, comparison is not straightforward because the confidence intervals of the previously reported values were not given and the analysis of the procedures used for the estimation of these values indicate that these intervals may be significant.

For D7, the activation energy was obtained from three experiments carried out at 50, 60 and 70 ºC.[1] In each experiment a value of k_D was estimated by fitting the evolution of the UV absorbance. The Arrhenius plot was constructed with these three values of k_D and the activation energy estimated from the slope of a straight line fitting the three points. Certainly, the value was indicative, but far from precise because a relatively narrow temperature range was used and, furthermore, in this range the values of k_D are small (actually the process cannot be carried at these temperatures) and therefore affected by uncertainty. Finally, as the Arrhenius plot only had three points the level of accuracy of the value is not high.

The activation energy for SG1 was not directly measured, but obtained through a lengthy process involving a number of assumptions. First, from an experiment carried out at 45 ºC, k_D and k_C were estimated by fitting the evolution of the conversion and M_n. No confidence intervals for the estimated parameters were given, but the predicted values of M_n were systematically about 20% below the experimental data (Figure 5 in *Macromol. Chem. Phys*. **2006**, 207, 1278–1288).[30] Therefore, the confidence intervals should be significant. Finally, assuming a frequency factor of 2.4x10^{14} taken from (*Macromolecules* **2000**, 33, 4403-4410)[31] the activation energy was estimated. It is worth pointing out that in *Macromolecules* **2000**, 33, 4403-4410,[31] it is stated that this value of the frequency factor was the average for several nitroxides and that there were deviations up to a factor of 2.5. Clearly, this casts doubts about the value of the activation energy reported.

For DPAIO, the value of k_D was not measured explicitly but estimated from the cleavage temperature (T_c) (*Macromolecules* **2007**, *40,* 3108-3114).[28] The method is based on the work of Le Mercier *et al.* (*Macromol Symp* **2002**, 182, 225-247).[32] In that work many different nitroxides and alkoxyamines were synthesized, k_D at 120 ºC was measured or obtained from other references, and a plot of log(k_D) was plotted vs T_c. was fit with one equation. While the general trend is clear, it should be noted that in some cases the measured values of k_D in this plot

are an order of magnitude away from the fit of the data, which can lead to significant errors in estimation of k_D from the cleavage temperature alone. The equation used to estimate k_D from T_c in *Macromolecules* **2007**, *40,* 3108-3114,[28] which is slightly different from that of Le Mercier *et al.*, is

$\log(k_{D,120^oC})=-0.057(\pm0.003)T_c+1.51\pm0.26$, where T_c is in ºC

This equation predicts that $1.07x10^{-4}$ s^{-1} < $k_{D,120^oC}$ < $3.55x10^{-4}$ s^{-1} namely, there is a huge uncertainty about the value of $k_{D,120^oC}$ that was later used (*Macromolecules* **2007**, *40,* 3108-3114)[28] to estimate the activation energy. This casts serious doubts about the accuracy of the activation energy reported.

References

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