Supporting Information

Transesterification or Polymerization? Kinetics of 2-(diethylamino)ethyl methacrylate in methanol and its competitive effect on free-radical polymerization

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Content

S.1. Reaction coordinate diagram and species

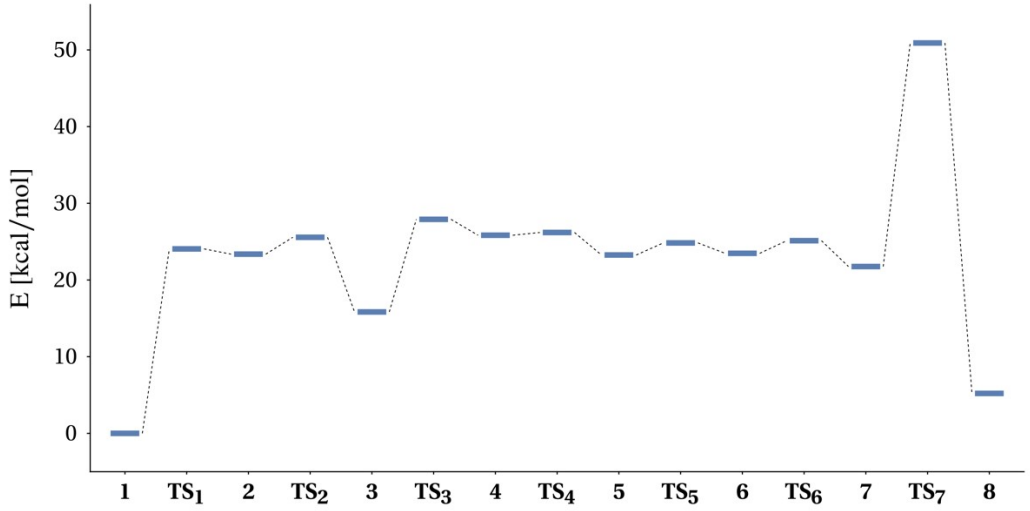

Figure S1. Reaction scheme for the transesterification process of DEAEMA with a methanol molecule, obtained from electronic structure calculations at the UB3LYP-PCM(methanol)/def2TZVP level of theory. Bold numbers denote minima (reactants, intermediaries and products) on the potential energy surface, while $\mathbf{TS_i}$ denotes the *i*-th transition state. Energies are referenced to 1.

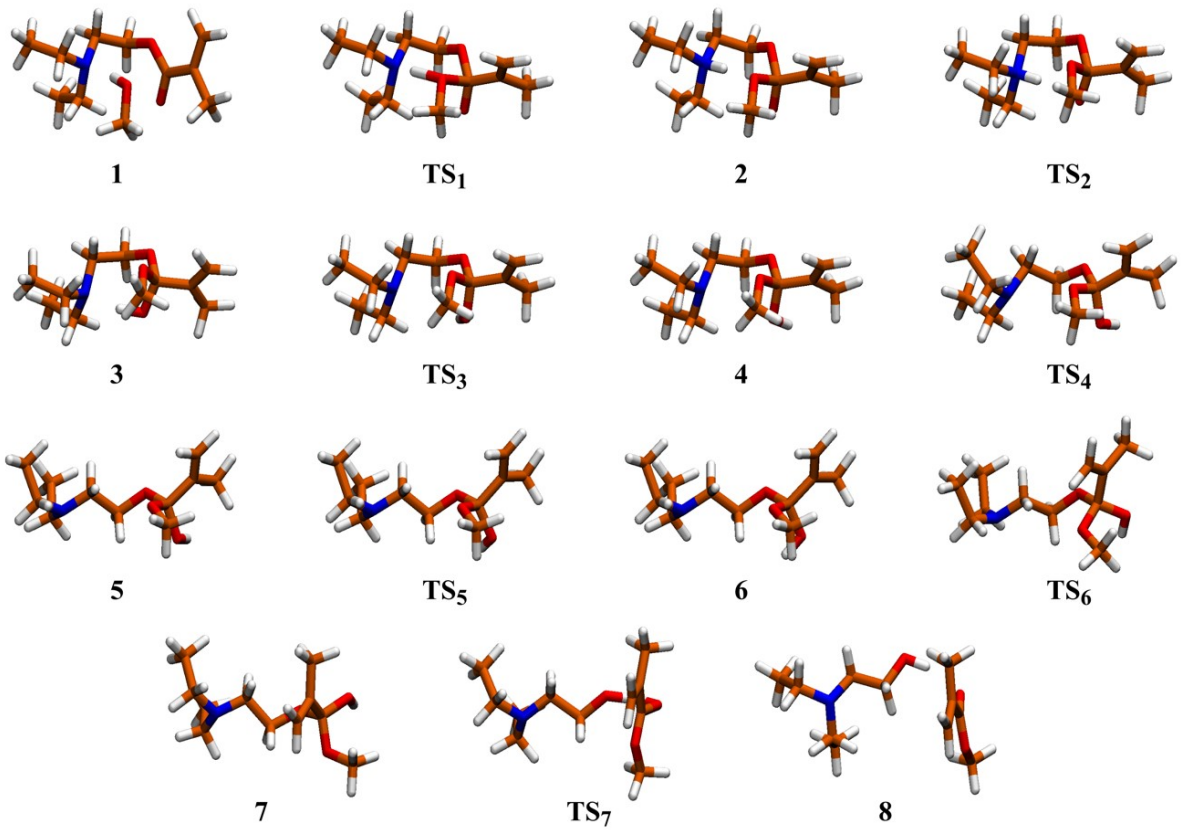

Figure S2. Molecular structures of the stationary points shown in the scheme of the transesterification reaction of DEAEMA with methanol (see Fig. S1).

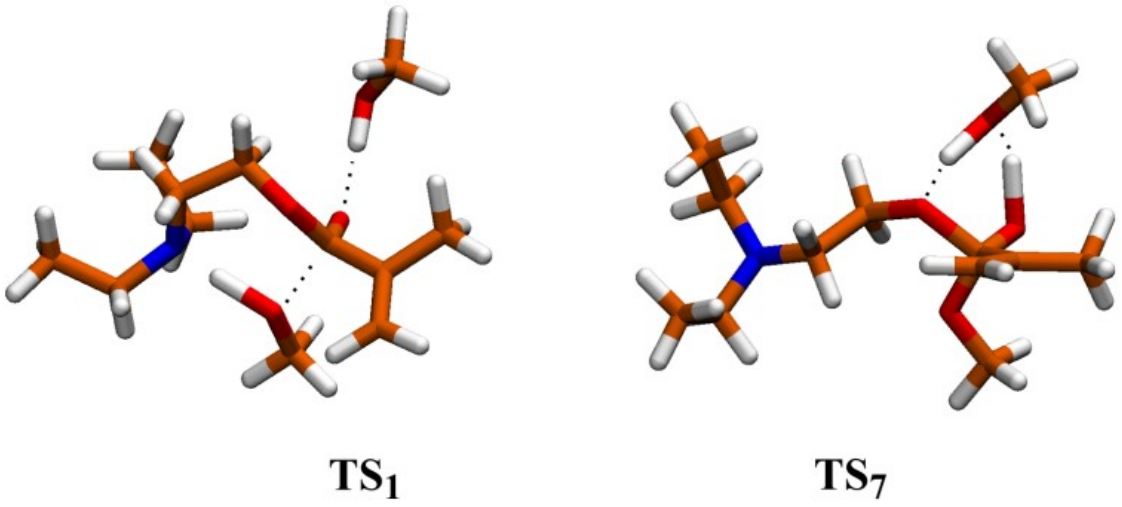

Figure S3. Molecular structures of the transition states analogous to $\mathbf{TS_1}$ and $\mathbf{TS_7}$ (see Fig. S2), considering two explicit solvent molecules.

S.2. Relevant molecular geometries for the DEAEMA-methanol transesterification reaction

Structure 1

EE -713.780734

C	3.388610	0.441234	-1.653310
C	3.017391	0.363960	-0.376246
C	3.723072	1.077599	0.736536
C	1.870645	-0.490876	0.043013
O	1.643127	-0.766476	1.202604
O	1.140999	-0.943190	-0.988687
C	0.043786	-1.841552	-0.729247
C	-1.281031	-1.189363	-1.073855
N	-1.668164	-0.110304	-0.170719
H	-0.382807	1.214923	-0.054711
C	-2.717808	0.752955	-0.730130
C	-1.866791	-0.512258	1.233578
C	-2.710405	-1.759549	1.507691
C	-4.098783	0.140183	-0.970995
O	0.206490	2.000708	0.050906
C	0.160606	2.407609	1.407829
H	0.794366	3.288656	1.516701
H	0.535421	1.626601	2.077584
H	-0.854360	2.676955	1.722508
H	2.860425	-0.090324	-2.431101
H	4.238303	1.044239	-1.947366
H	4.546984	1.673718	0.347535
H	3.033536	1.734308	1.269266
H	4.115342	0.368939	1.468023
H	0.198943	-2.697739	-1.384619
H	0.088622	-2.172948	0.304382
H	-2.028315	-1.992537	-1.119393
H	-1.209688	-0.771571	-2.079791
H	-2.331527	1.137728	-1.677213
H	-2.816831	1.612114	-0.063328
H	-2.309105	0.345504	1.742109
H	-0.880412	-0.658470	1.677379
H	-2.255627	-2.658656	1.089885
H	-3.720897	-1.679033	1.111147
H	-2.782728	-1.904964	2.587185
H	-4.724284	0.861858	-1.500252
H	-4.601362	-0.110373	-0.037517
H	-4.041745	-0.760813	-1.583540

Structure TS1

EE -713.742406 i -272.96 cm^-1

C	3.056869	1.820747	-0.900536
C	2.900726	0.728524	-0.160645
C	4.064184	-0.071139	0.354758
C	1.554651	0.150380	0.253011
O	1.389045	-0.223878	1.429077
O	1.154184	-0.719644	-0.814542
C	0.148014	-1.673383	-0.514358
C	-1.229719	-1.199484	-0.951140
N	-1.697747	-0.023261	-0.163878
H	-0.817382	0.662410	-0.143935
C	-2.772482	0.752442	-0.856702
C	-1.970088	-0.312224	1.289063
C	-2.689769	-1.613890	1.598607
C	-4.102239	0.041686	-1.029851
O	0.399412	1.445183	-0.090204
C	0.342159	2.407409	0.934739
H	1.118557	3.170386	0.806428
H	0.473946	1.942747	1.918307
H	-0.631768	2.908171	0.917991
H	2.207766	2.382355	-1.259556
H	4.047811	2.176331	-1.159141
H	5.010463	0.347616	0.012730
H	4.059280	-0.093979	1.445964
H	4.000067	-1.109430	0.017728
H	0.381387	-2.575521	-1.081412
H	0.175196	-1.917033	0.547710
H	-1.951179	-2.009914	-0.873012
H	-1.185692	-0.881699	-1.991913
H	-2.357447	1.028433	-1.825631
H	-2.900341	1.670032	-0.283415
H	-2.537684	0.539605	1.660088
H	-0.994813	-0.298267	1.773702
H	-2.083378	-2.485697	1.356224
H	-3.645368	-1.705752	1.086908
H	-2.882232	-1.641141	2.671686

H	-4.754030	0.674695	-1.632516
H	-4.599858	-0.131259	-0.077281
H	-3.994263	-0.910709	-1.548515
H	-4.807158	0.458934	-1.680403
H	-4.617344	-0.306300	-0.108928
H	-4.008061	-1.105088	-1.568993

Structure 2

EE -713.743494

C	3.134927	1.749891	-0.885019
C	2.889138	0.644018	-0.188728
C	3.983034	-0.272516	0.275066
C	1.485874	0.185264	0.215992
O	1.341027	-0.262148	1.392316
O	1.109846	-0.740945	-0.891052
C	0.163521	-1.734317	-0.567961
C	-1.242330	-1.332263	-0.991466
N	-1.724191	-0.138140	-0.229058
H	-0.891072	0.527146	-0.229691
C	-2.823115	0.604106	-0.931105
C	-1.976585	-0.393706	1.240766
C	-2.667130	-1.700387	1.585967
C	-4.134408	-0.144334	-1.070670
O	0.491568	1.342481	-0.095963
C	0.422947	2.324742	0.924872
H	1.314323	2.958564	0.921589
H	0.324784	1.860560	1.908136
H	-0.451316	2.947569	0.728624
H	2.337107	2.397299	-1.219274
H	4.149652	2.034026	-1.140776
H	4.959760	0.076067	-0.061300
H	3.986296	-0.345348	1.363745
H	3.822720	-1.284409	-0.106398
H	0.423011	-2.640769	-1.119639
H	0.211354	-1.957648	0.499603
H	-1.943735	-2.152374	-0.862035
H	-1.235382	-1.045527	-2.041885
H	-2.421730	0.862871	-1.910025
H	-2.963934	1.530421	-0.375924
H	-2.555533	0.458738	1.591504
H	-0.992427	-0.350950	1.705967
H	-2.041773	-2.564523	1.366086
H	-3.623258	-1.827665	1.083188
H	-2.853669	-1.700239	2.660382

Structure TS2

EE -713.739993 i -87.39 cm^-1

C	3.515004	1.113523	-1.197169
C	3.014831	0.195167	-0.375709
C	3.881998	-0.789999	0.349975
C	1.515499	0.039153	-0.099941
O	1.175826	-0.261025	1.098034
O	1.096731	-0.946878	-1.138709
C	0.017230	-1.781714	-0.788792
C	-1.341739	-1.112643	-0.954877
N	-1.611945	-0.110090	0.130821
H	-0.703866	0.379636	0.233505
C	-2.577334	0.961868	-0.291705
C	-1.895964	-0.708676	1.491901
C	-2.763028	-1.953388	1.507030
C	-3.988354	0.486409	-0.571756
O	0.773651	1.257830	-0.599681
C	0.877059	2.384081	0.256437
H	1.899287	2.771612	0.292771
H	0.562982	2.142679	1.275707
H	0.220876	3.156021	-0.147268
H	4.582640	1.186849	-1.372162
H	2.876460	1.813588	-1.717366
H	4.930246	-0.671722	0.074024
H	3.783039	-0.666880	1.429637
H	3.574103	-1.813959	0.122688
H	0.044536	-2.629186	-1.475925
H	0.138577	-2.161681	0.228158
H	-2.144521	-1.843662	-0.962336
H	-1.359211	-0.565454	-1.895115
H	-2.133028	1.416030	-1.175720
H	-2.567770	1.704534	0.504593
H	-2.350956	0.091009	2.073367
H	-0.913430	-0.911602	1.909593

H	-2.263386	-2.807614	1.052352
H	-3.725076	-1.812855	1.018641
H	-2.954255	-2.206639	2.550265
H	-4.561868	1.331847	-0.951724
H	-4.485633	0.128553	0.327839
H	-4.015746	-0.298384	-1.327000
H	-2.478194	1.513308	1.233315
H	-2.407971	-0.426928	2.392691
H	-1.181365	-1.596673	1.973727
H	-2.800996	-2.932993	0.657150
H	-4.072387	-1.747258	0.958394
H	-3.373128	-2.660214	2.295869
H	-4.358549	1.777434	-0.407058
H	-4.548539	0.318978	0.561335
H	-3.976344	0.205085	-1.108181

Structure 3

EE -713.755502

C	3.628626	1.058119	-1.045775
C	2.931112	0.295216	-0.212445
C	3.567581	-0.622343	0.787990
C	1.407627	0.249186	-0.272817
O	0.901098	0.159162	1.004447
O	1.097688	-0.873902	-1.082348
C	-0.043587	-1.676762	-0.761888
C	-1.386953	-0.951921	-0.783827
N	-1.679861	-0.239654	0.467171
H	-0.108706	0.134712	0.910459
C	-2.484133	0.974945	0.283006
C	-2.079235	-1.098304	1.598265
C	-3.146555	-2.165077	1.349868
C	-3.925824	0.798054	-0.193494
O	0.840758	1.350032	-0.972455
C	0.847408	2.595204	-0.280339
H	1.850812	2.864027	0.056029
H	0.177403	2.579432	0.580672
H	0.497242	3.339286	-0.993436
H	4.711490	1.051524	-1.032524
H	3.142308	1.703434	-1.763845
H	4.652125	-0.616687	0.683449
H	3.310667	-0.327488	1.806677
H	3.208769	-1.645835	0.655051
H	-0.046087	-2.442381	-1.536494
H	0.111818	-2.176067	0.197805
H	-2.164652	-1.682127	-1.027485
H	-1.367882	-0.222080	-1.591942
H	-1.943829	1.595070	-0.434169

Structure TS3

EE -713.736262 i -380.83 cm^-1

C	3.471475	1.296967	-1.342978
C	3.085206	0.324531	-0.525791
C	4.039627	-0.645335	0.105232
C	1.605429	0.114329	-0.189374
O	1.472275	0.015222	1.214007
O	1.238427	-1.055827	-0.857095
C	0.032463	-1.763931	-0.521671
C	-1.287050	-1.051438	-0.798021
N	-1.744697	-0.184648	0.270378
H	1.185145	-0.872226	1.451462
C	-2.559612	0.935518	-0.168911
C	-2.141753	-0.834259	1.511474
C	-3.165834	-1.974602	1.432488
C	-3.940766	0.622168	-0.759989
O	0.799314	1.152069	-0.672585
C	0.661026	2.299942	0.156694
H	1.630442	2.670931	0.497516
H	0.030220	2.081547	1.017368
H	0.185765	3.060226	-0.460128
H	4.517200	1.433382	-1.589603
H	2.759701	1.977467	-1.787636
H	5.053270	-0.486115	-0.260733
H	4.040627	-0.539824	1.191583
H	3.747020	-1.674251	-0.115704
H	0.092561	-2.649475	-1.152582
H	0.071661	-2.120619	0.512799

H	-2.018306	-1.835480	-1.050127
H	-1.159921	-0.448075	-1.696607
H	-1.975067	1.479016	-0.915717
H	-2.681232	1.611230	0.682007
H	-2.524894	-0.051482	2.169261
H	-1.246474	-1.224293	2.007859
H	-2.791364	-2.813042	0.842891
H	-4.108949	-1.650408	0.993892
H	-3.370155	-2.348466	2.438178
H	-4.393833	1.537446	-1.148647
H	-4.617311	0.207888	-0.012210
H	-3.868171	-0.089742	-1.584611

Structure 4

EE -713.739563

C	3.399135	1.370051	-1.231955
C	2.999328	0.373601	-0.451802
C	3.948926	-0.631293	0.136165
C	1.513706	0.171460	-0.134294
O	1.308826	-0.004885	1.247648
O	1.130407	-0.953994	-0.875325
C	-0.040572	-1.692743	-0.486841
C	-1.380759	-1.019309	-0.766658
N	-1.836593	-0.114641	0.269318
H	1.977710	-0.609826	1.588733
C	-2.676741	0.972983	-0.195014
C	-2.168632	-0.708310	1.553994
C	-3.190836	-1.853750	1.572742
C	-4.058737	0.614537	-0.759825
O	0.722660	1.238410	-0.556116
C	0.604955	2.354527	0.319083
H	1.577813	2.677680	0.695270
H	-0.052771	2.121906	1.155819
H	0.167521	3.155003	-0.274842
H	4.446140	1.500536	-1.475831
H	2.695818	2.075843	-1.649907
H	4.949500	-0.502515	-0.273664
H	4.030450	-0.527558	1.222909
H	3.617960	-1.650835	-0.072760
H	0.026714	-2.597196	-1.090999
H	0.040106	-1.982475	0.560792
H	-2.102701	-1.827063	-0.970871
H	-1.285311	-0.453751	-1.694474
H	-2.112427	1.505747	-0.966096
H	-2.802776	1.673252	0.635459
H	-2.526309	0.100829	2.194886
H	-1.244286	-1.069443	2.015384
H	-2.846995	-2.709146	0.988564
H	-4.159851	-1.546729	1.179841
H	-3.335156	-2.196656	2.599931
H	-4.538135	1.508339	-1.166926
H	-4.715587	0.204111	0.007513
H	-3.979619	-0.117583	-1.566010

Structure TS4

EE -713.738997 i -37.94 cm^-1

C	3.140882	1.231054	-1.760275
C	3.105166	0.338152	-0.779135
C	4.280208	-0.522531	-0.414566
C	1.819965	0.108278	0.019868
O	2.081616	0.027840	1.407722
O	1.288551	-1.085771	-0.475382
C	0.106760	-1.603622	0.167993
C	-1.199518	-1.059288	-0.431663
N	-1.987395	-0.289869	0.517973
H	2.742262	-0.658910	1.557821
C	-2.720278	0.829503	-0.055057
C	-2.663375	-1.072097	1.542976
C	-3.813086	-1.995108	1.112569
C	-3.721336	0.534843	-1.181321
O	0.868050	1.109697	-0.154107
C	1.063001	2.330346	0.556849
H	2.073360	2.719230	0.417016
H	0.869292	2.199860	1.621231
H	0.345886	3.034552	0.140025
H	4.039602	1.379175	-2.345830

H	2.278335	1.833188	-2.008296
H	5.088751	-0.396196	-1.132848
H	4.673733	-0.267079	0.573383
H	4.000929	-1.578780	-0.394569
H	0.182163	-2.681425	0.028362
H	0.151254	-1.388949	1.234455
H	-1.768856	-1.892766	-0.867625
H	-0.929589	-0.404709	-1.257640
H	-1.977507	1.535753	-0.439186
H	-3.238605	1.333902	0.764816
H	-3.033692	-0.374156	2.298886
H	-1.904919	-1.683225	2.040972
H	-3.514005	-2.661060	0.301318
H	-4.685344	-1.430999	0.784467
H	-4.117618	-2.618200	1.956734
H	-4.125585	1.474060	-1.566731
H	-4.557039	-0.076571	-0.843899
H	-3.238553	0.018212	-2.012938
H	1.979252	2.785932	1.456233
H	1.387663	3.582264	-0.022067
H	3.852600	0.597274	-2.770742
H	2.397691	1.606875	-2.237586
H	4.587080	-1.262504	-1.459009
H	4.563686	-0.833961	0.250164
H	3.375393	-1.971396	-0.384001
H	-0.353300	-1.636474	1.119625
H	-0.076125	0.048323	1.571004
H	-1.482441	-0.833973	-0.989055
H	-1.236025	0.821798	-0.452705
H	-3.231574	1.712186	0.098517
H	-4.465606	0.779813	0.923495
H	-4.086678	-1.307916	1.636978
H	-2.448189	-1.790708	1.995536
H	-2.230432	-2.869787	-0.251649
H	-3.884169	-2.401675	-0.645431
H	-3.571088	-3.519498	0.684832
H	-4.971183	1.171739	-1.500784
H	-4.893881	-0.550480	-1.133432
H	-3.543996	0.239635	-1.956762

Structure 5

EE -713.743671

C	3.086566	0.799673	-2.032736
C	3.000176	0.076179	-0.923555
C	3.931972	-1.059228	-0.613387
C	1.893693	0.343298	0.098524
O	2.395011	0.330483	1.423170
O	0.952974	-0.668003	-0.098960
C	-0.222769	-0.626571	0.729690
C	-1.423766	-0.191653	-0.097867
N	-2.644728	-0.174985	0.690184
H	2.794064	-0.531743	1.590368
C	-3.676121	0.715245	0.170001
C	-3.107812	-1.472792	1.182346
C	-3.204403	-2.625577	0.175679
C	-4.305142	0.365479	-1.184561
O	1.252599	1.569367	-0.073214
C	1.948860	2.735939	0.368231
H	2.966400	2.765409	-0.024803

Structure TS5

EE -713.741164 i -319.10 cm^-1

C	3.015016	0.879913	-2.050076
C	2.972594	0.089825	-0.984125
C	3.879807	-1.089434	-0.797145
C	1.942071	0.316633	0.121023
O	2.603435	0.259202	1.375478
O	1.004561	-0.706834	-0.005093
C	-0.193412	-0.608775	0.789800
C	-1.371131	-0.215920	-0.090311
N	-2.609384	-0.152607	0.666392
H	2.166341	-0.400943	1.924882
C	-3.619751	0.722292	0.082338
C	-3.096274	-1.422002	1.207859
C	-3.179204	-2.620041	0.254462
C	-4.221828	0.314415	-1.267980

O	1.261665	1.536620	0.002402
C	1.935696	2.701438	0.475220
H	2.937402	2.785467	0.049220
H	2.006180	2.700033	1.562580
H	1.334449	3.546772	0.147317
H	3.729075	0.702206	-2.844460
H	2.340951	1.716737	-2.163947
H	4.506398	-1.238525	-1.675672
H	4.522497	-0.951628	0.073779
H	3.299809	-1.998796	-0.624145
H	-0.339112	-1.594386	1.232135
H	-0.073182	0.117372	1.593622
H	-1.408186	-0.907682	-0.944651
H	-1.169016	0.775323	-0.495363
H	-3.163319	1.710493	-0.025445
H	-4.424675	0.829354	0.814235
H	-4.084183	-1.227509	1.629850
H	-2.459908	-1.706440	2.051491
H	-2.197369	-2.893965	-0.135214
H	-3.835139	-2.428578	-0.593784
H	-3.568589	-3.485166	0.795419
H	-4.873100	1.110346	-1.636682
H	-4.820023	-0.593229	-1.187118
H	-3.444909	0.146005	-2.016019

C	-3.093914	-1.460048	1.190967
C	-3.184047	-2.637390	0.212745
C	-4.312788	0.311990	-1.212717
O	1.327949	1.558085	0.039843
C	2.099630	2.679295	0.471772
H	3.080133	2.696846	-0.006057
H	2.227960	2.682261	1.554972
H	1.536923	3.561238	0.173683
H	3.758979	0.637366	-2.840805
H	2.346034	1.641200	-2.195503
H	4.578091	-1.243357	-1.607709
H	4.562711	-0.924751	0.135993
H	3.372774	-2.010103	-0.558014
H	-0.335438	-1.618137	1.115612
H	-0.096736	0.081540	1.532755
H	-1.481364	-0.862002	-1.003863
H	-1.236767	0.805122	-0.501897
H	-3.238149	1.697051	0.028270
H	-4.463173	0.781400	0.884532
H	-4.073246	-1.289910	1.642444
H	-2.431540	-1.753416	2.011136
H	-2.208559	-2.888022	-0.207401
H	-3.863762	-2.436565	-0.614311
H	-3.547378	-3.520101	0.743290
H	-4.983905	1.106874	-1.546398
H	-4.897575	-0.604538	-1.133811
H	-3.555624	0.168655	-1.985778

Structure 6

EE -713.743322

C	3.037624	0.822421	-2.055024
C	3.006751	0.062956	-0.967140
C	3.935599	-1.092047	-0.741077
C	1.947321	0.297658	0.105433
O	2.570368	0.114304	1.355487
O	0.949997	-0.651613	-0.134382
C	-0.215682	-0.616011	0.702743
C	-1.422625	-0.201646	-0.126225
N	-2.639542	-0.171475	0.666222
H	1.927143	0.292356	2.054149
C	-3.677920	0.700500	0.128333

Structure TS6

EE -713.740699 i -38.33 cm^-1

C	1.507234	2.032930	-1.775497
C	2.133520	0.936491	-1.365496
C	3.018253	0.114908	-2.254494
C	1.915030	0.396253	0.046723
O	3.168263	-0.007180	0.538524
O	1.080471	-0.735894	-0.068209
C	-0.068922	-0.891846	0.773798
C	-1.284781	-0.178460	0.194645

N	-2.467290	-0.381228	1.014100
H	3.016306	-0.514433	1.347868
C	-3.476574	0.661715	0.872079
C	-2.969080	-1.753689	1.086335
C	-3.167045	-2.511848	-0.231877
C	-4.178501	0.794926	-0.485231
O	1.300790	1.308602	0.908670
C	2.120151	2.361743	1.415755
H	2.656023	2.872217	0.614473
H	2.836837	1.986702	2.146393
H	1.439657	3.060015	1.897977
H	1.618397	2.387550	-2.792375
H	0.861733	2.599144	-1.119083
H	3.013559	0.506318	-3.271181
H	4.045002	0.107281	-1.885367
H	2.682307	-0.924123	-2.277924
H	-0.229246	-1.969210	0.807454
H	0.126936	-0.541924	1.786157
H	-1.408529	-0.502564	-0.849236
H	-1.072562	0.889825	0.170143
H	-2.988579	1.612790	1.104496
H	-4.229048	0.500050	1.648507
H	-3.916853	-1.716423	1.627051
H	-2.288733	-2.339288	1.712275
H	-2.226318	-2.634081	-0.771267
H	-3.871230	-2.011073	-0.895069
H	-3.553742	-3.510843	-0.019139
H	-4.818248	1.680588	-0.484377
H	-4.807299	-0.068546	-0.702612
H	-3.457261	0.905254	-1.297134

O	1.180577	-0.802670	0.109771
C	-0.079535	-0.525690	0.739085
C	-1.185104	-0.503607	-0.307007
N	-2.485864	-0.250618	0.287669
H	3.451882	-1.127146	-0.147828
C	-3.458744	0.325930	-0.633274
C	-2.990628	-1.286023	1.189975
C	-2.970065	-2.736787	0.693865
C	-3.925458	-0.537814	-1.811628
O	2.408546	0.587480	1.382577
C	3.570309	1.389211	1.594864
H	3.557980	2.288342	0.976918
H	4.480207	0.824584	1.387496
H	3.550834	1.673686	2.644734
H	0.675021	3.284506	-0.814375
H	1.116306	2.626161	0.854684
H	1.063132	1.987152	-2.779769
H	2.616110	1.140251	-2.667459
H	1.122685	0.233395	-2.525210
H	-0.238690	-1.318772	1.470130
H	-0.047659	0.421956	1.273329
H	-1.135642	-1.437512	-0.886057
H	-0.975471	0.308035	-1.004534
H	-3.017240	1.244686	-1.030488
H	-4.329259	0.628092	-0.045204
H	-4.013882	-1.007740	1.449732
H	-2.420422	-1.240825	2.122777
H	-1.954044	-3.077487	0.487700
H	-3.559619	-2.872294	-0.211958
H	-3.382401	-3.388559	1.467105
H	-4.558255	0.055672	-2.475662
H	-4.507528	-1.397144	-1.478667
H	-3.079820	-0.904124	-2.396645

Structure 7

EE -713.746071

C	1.108899	2.492205	-0.217615
C	1.604125	1.401593	-0.791306
C	1.598799	1.183986	-2.275107
C	2.124159	0.239446	0.048303
O	3.240848	-0.293200	-0.591550

Structure TS7

EE -713.699612 i -1069.65 cm^-1

C	2.142651	2.988710	-1.311763
C	2.409670	1.688700	-1.446365

C	2.624920	1.016150	-2.768583
C	2.530689	0.825428	-0.252863
O	3.208975	-0.301034	-0.296357
O	0.967039	-0.436002	-0.528617
C	-0.116667	-0.372024	0.350350
C	-1.438994	-0.379180	-0.414413
N	-2.596392	-0.197621	0.447350
H	2.278225	-0.879285	-0.340653
C	-3.785182	0.287849	-0.242814
C	-2.817629	-1.243519	1.445043
C	-2.818398	-2.700581	0.965581
C	-4.438912	-0.632214	-1.282450
O	2.317080	1.411988	0.901062
C	2.619826	0.682962	2.112023
H	3.684045	0.466657	2.156564
H	2.048081	-0.240833	2.150362
H	2.325148	1.346031	2.918298
H	2.060019	3.626551	-2.181806
H	2.004434	3.445073	-0.342567
H	2.486402	1.726407	-3.581710
H	3.631097	0.599018	-2.834414
H	1.922666	0.191094	-2.891432
H	-0.080129	-1.206121	1.064549
H	-0.069565	0.552345	0.948466
H	-1.481988	-1.297384	-1.020221
H	-1.414716	0.455831	-1.118920
H	-3.507438	1.223593	-0.737279
H	-4.526276	0.546261	0.518607
H	-3.770553	-1.023524	1.931252
H	-2.052234	-1.146205	2.220806
H	-1.860487	-2.976806	0.521808
H	-3.597422	-2.893731	0.229239
H	-2.987337	-3.362002	1.818269
H	-5.238640	-0.095394	-1.798282
H	-4.877139	-1.517652	-0.821940
H	-3.718389	-0.959603	-2.034084

Structure 8

EE -713.772436

C	2.433341	3.133056	-0.223389
C	2.561429	1.978896	-0.878079
C	2.374781	1.838935	-2.359824
C	2.885407	0.723492	-0.148374
O	2.866753	-0.377103	-0.673869
O	0.389087	-1.132603	-1.809452
C	-0.406119	-0.433532	-0.855929
C	-1.853339	-0.852208	-1.052834
N	-2.765755	-0.098347	-0.210336
H	1.319027	-0.975979	-1.577944
C	-4.145874	-0.095182	-0.680626
C	-2.578428	-0.254833	1.231748
C	-2.500094	-1.680329	1.792080
C	-4.908329	-1.426524	-0.678529
O	3.198394	0.898408	1.135228
C	3.468845	-0.291540	1.900340
H	4.327378	-0.818114	1.487753
H	2.599887	-0.947242	1.894915
H	3.680565	0.054839	2.906776
H	2.183732	4.043884	-0.752109
H	2.567842	3.197639	0.846338
H	2.163097	2.807751	-2.808452
H	3.269896	1.423325	-2.826698
H	1.553251	1.159191	-2.591844
H	-0.067510	-0.667355	0.158477
H	-0.324003	0.651402	-0.992808
H	-1.920991	-1.941626	-0.913250
H	-2.120620	-0.654942	-2.093826
H	-4.133872	0.294402	-1.702932
H	-4.696751	0.631219	-0.077282
H	-3.397118	0.279719	1.717866
H	-1.662325	0.270482	1.518454
H	-1.659420	-2.232732	1.368929
H	-3.407519	-2.251035	1.599497
H	-2.351275	-1.635972	2.873175
H	-5.879016	-1.295097	-1.162401
H	-5.088578	-1.789130	0.333427
H	-4.365100	-2.198684	-1.226220

S.3. Relevant molecular geometries for the DEAEMA-methanol transesterification reaction

TS1 - analog

EE -829.276232 i -334.00 cm^-1

C	3.034439	1.768092	-0.980088
C	2.920353	0.710368	-0.171222
C	4.112082	-0.003912	0.417872
C	1.594476	0.088447	0.235630
O	1.406140	-0.241374	1.433935
O	1.183407	-0.769031	-0.800278
C	0.131337	-1.699706	-0.520024
C	-1.228986	-1.174845	-0.964837
N	-1.689573	-0.010578	-0.153752
H	-0.777878	0.700854	-0.133298
C	-2.773159	0.773814	-0.829152
C	-1.954454	-0.326194	1.296628
C	-2.673192	-1.639889	1.588701
C	-4.110598	0.064026	-1.001873
O	0.367594	1.447719	-0.115986
C	0.334417	2.415565	0.913090
H	1.123394	3.165923	0.766818
H	0.475601	1.947494	1.897851
H	-0.635293	2.931878	0.910548
H	2.158015	2.262664	-1.379739
H	4.013623	2.159648	-1.243302
H	5.045611	0.461866	0.092076
H	4.070353	0.009745	1.511770
H	4.124990	-1.057599	0.114744
H	0.354059	-2.593410	-1.107508
H	0.140767	-1.969612	0.537225
H	-1.964727	-1.980512	-0.919602
H	-1.161924	-0.832955	-2.000187
H	-2.365745	1.064446	-1.801082
H	-2.897544	1.686927	-0.241433
H	-2.524247	0.519946	1.687005
H	-0.976339	-0.318601	1.783174
H	-2.065008	-2.509889	1.328917
H	-3.633021	-1.724519	1.076345
H	-2.862268	-1.686771	2.665118
H	-4.768949	0.707138	-1.592933
H	-4.602065	-0.121259	-0.044386
H	-4.008028	-0.884941	-1.535211
C	2.697031	-3.381314	1.799934
H	2.749675	-4.405470	2.179133
H	2.418165	-3.419204	0.737789
H	3.695128	-2.929626	1.879593
O	1.732833	-2.678303	2.575979
H	1.625881	-1.781446	2.184430

TS7 - analog

EE -829.503122 i -1139.15 cm^-1

C	2.333904	-0.479765	-1.827950
C	2.831704	-0.173833	-0.634655
C	4.305258	-0.041963	-0.380566
C	1.928848	0.106018	0.572704
O	2.479190	-0.043222	1.741497
O	0.757224	-0.997740	0.412207
C	-0.510287	-0.690225	1.032972
C	-1.496250	-0.220990	-0.024007
N	-2.786867	0.104014	0.556425
H	2.446383	-1.394725	1.971167
C	-3.571801	1.049556	-0.228893
C	-3.525636	-1.015194	1.141595
C	-3.691764	-2.282166	0.293856
C	-4.069014	0.593107	-1.606108
O	1.189394	1.289885	0.409414
C	1.948744	2.483780	0.570875
H	2.660383	2.611208	-0.250045
H	2.483466	2.483534	1.521558
H	1.235611	3.304757	0.553130
H	2.984758	-0.646322	-2.677697
H	1.269983	-0.579873	-1.989200
H	4.868355	-0.200927	-1.299639
H	4.553262	0.945435	0.014983
H	4.641295	-0.762764	0.366946
H	-0.845111	-1.611482	1.511043
H	-0.374268	0.069337	1.801077

H	−1.545488	−0.984145	−0.814777	H	−4.538952	1.431943	−2.124845
H	−1.091713	0.681969	−0.479802	H	−4.808211	−0.204009	−1.526343
H	−2.955888	1.943760	−0.361154	H	−3.246505	0.235198	−2.228158
H	−4.429417	1.349357	0.379009	C	2.963269	−3.334630	1.284684
H	−4.510530	−0.634187	1.418421	H	3.780786	−3.484218	1.987736
H	−3.038636	−1.298982	2.079744	H	3.357397	−2.964433	0.336818
H	−2.728691	−2.735575	0.053111	H	2.449459	−4.279284	1.119314
H	−4.214069	−2.087711	−0.641982	O	2.026259	−2.404034	1.850216
H	−4.267923	−3.019764	0.856563	H	1.296728	−1.902592	1.054378

S.4. ^{1}H-NMR Spectra and Peak Assignments

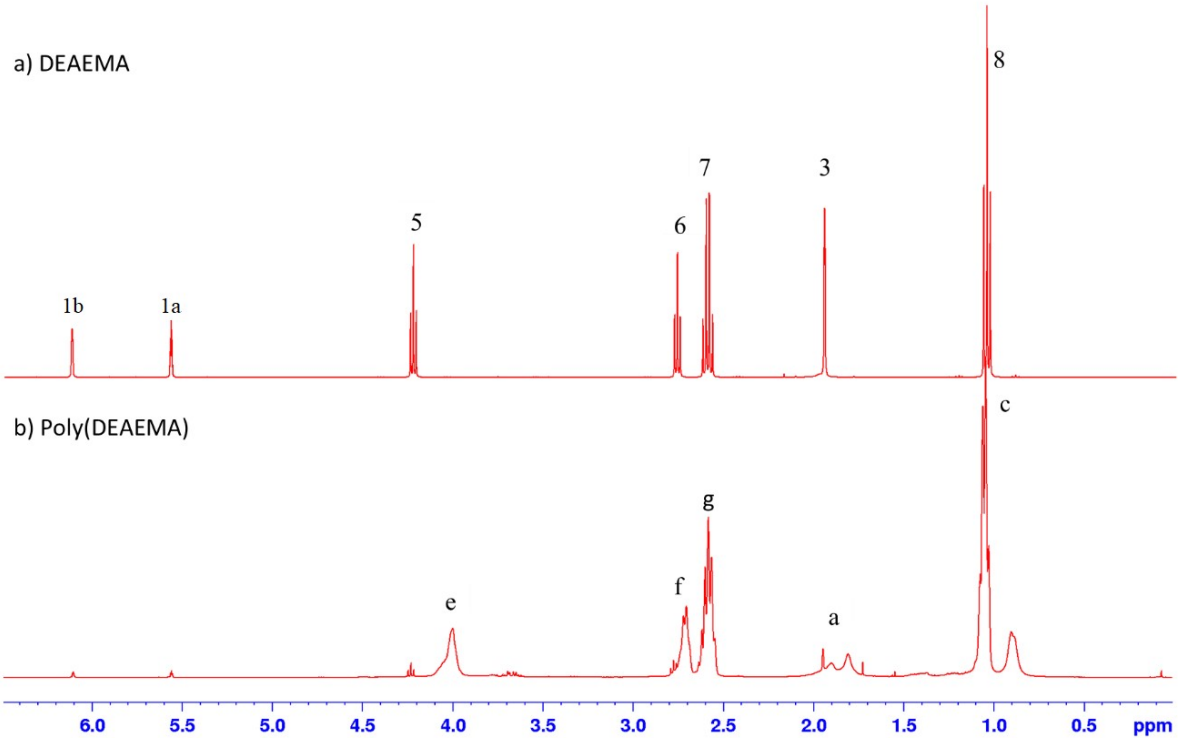

Figure S4. ^{1}H-NMR (400 MHz) spectra in CD_3Cl at 26.80 °C of: a) DEAEMA monomer and b) poly(DEAEMA). The peak assignations correspond to the structures shown in Scheme 1 and 2.

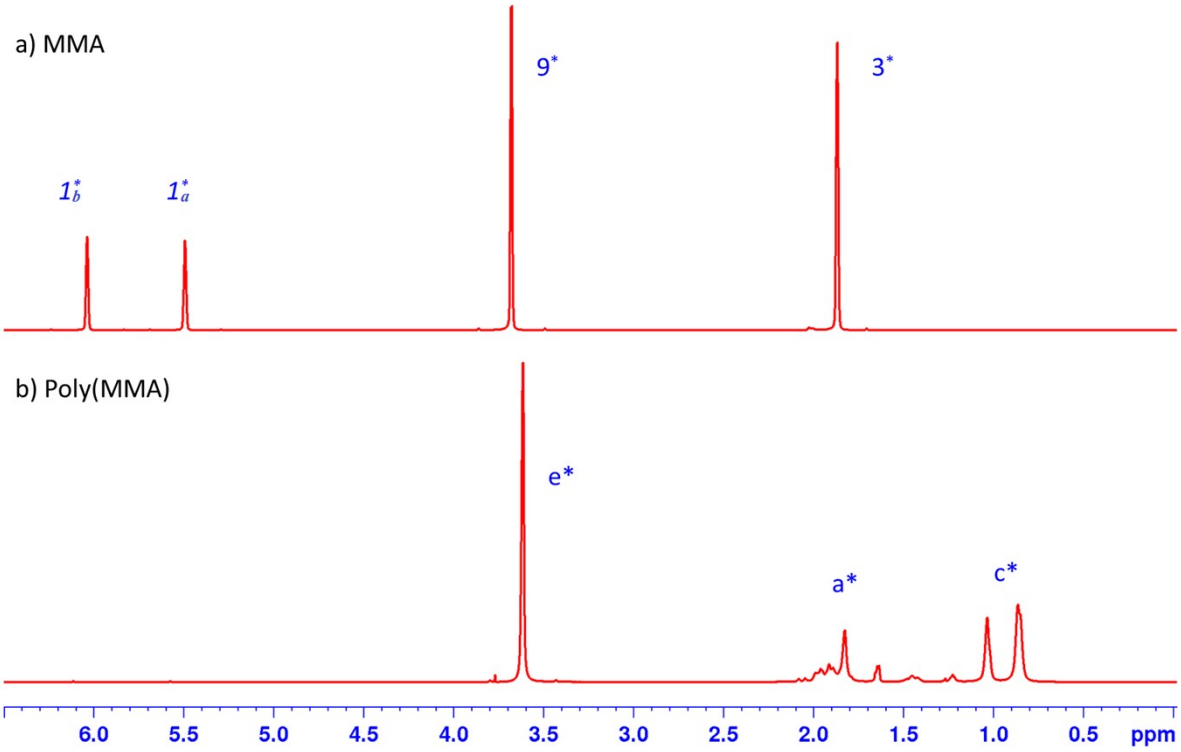

Figure S5. a) MMA monomer and b) Poly(MMA) spectra of ^{1}H-NMR in CD_3Cl at 300 K. The peak assignations correspond to the structures shown in Scheme 1 and 2.

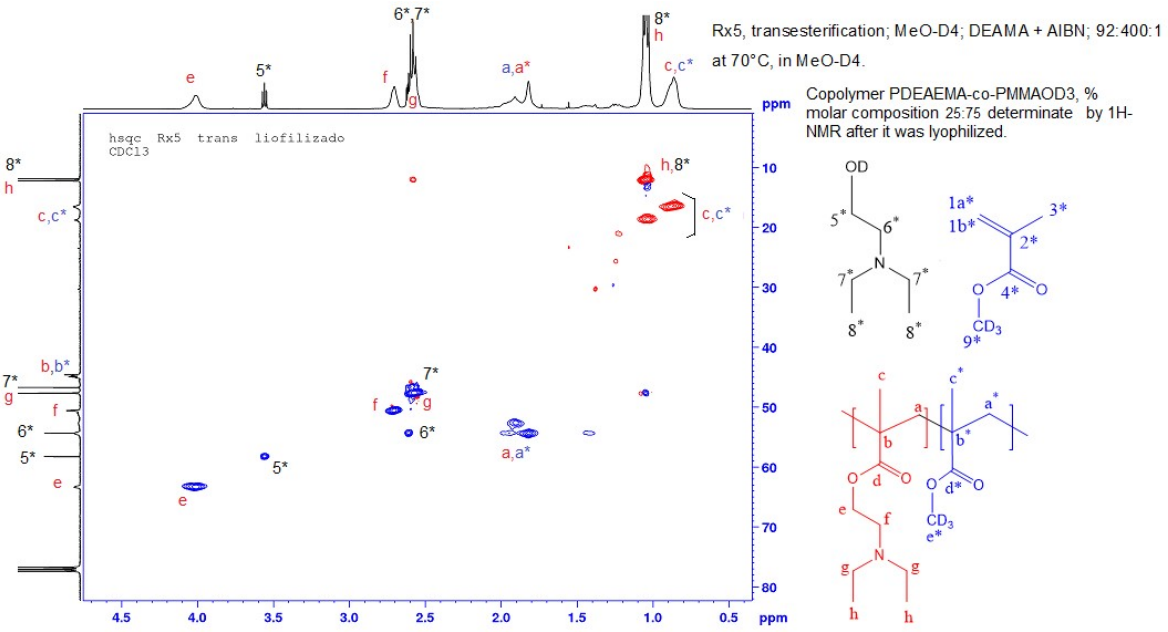

Figure S6. a) Edited HSQC (400MHz, $CDCl_3$, r.t.) of copolymer Poly(DEAEMA-co-MMA-OD_3), % molar composition 25:75 determinate by ^{1}H-NMR after it was lyophilized at the end of kinetic.

S.5. Kinetic study using a *pseudo*-first-order reaction.

A *pseudo*-first-order reaction is used to the kinetic analysis of the transesterification, and the apparent rate coefficients ($k_{obs} = k_{tran}[CD_3OD]_0$) are estimated using the following expression, Equation (S1):

$$ln\left(\frac{[DEAEMA]}{[DEAEMA]_0}\right) = k_{tran}[CD_3OD]_0 t = k_{obs} t \quad \text{(S1)}$$

$$ln\left(k_{obs}\right) = ln(A) - \frac{E_A}{RT} \quad \text{(S2)}$$

where k_{obs} (s^{-1}) denotes the observed rate coefficients, A (s^{-1}) is the preexponential factor, E_A (kJ mol^{-1}) is the activation energy, T (K) is the temperature. **Figure S7** shows the plots and the linear regressions where the slops are proportional to the estimated value of k_{obs} showed in **Table S1**. A nonlinear behavior is seen for the experiments at high temperatures (60 and 70 °C) and low values of ω_{M0} (10 and 30 wt%). **Table S1** also shows the half-lives ($\tau_{1/2}$) of each reaction condition. For the experiment with ω_{M0} = 10 wt% and T = 70 °C, the half of initial concentration of DEAEMA is converted to MMA-*d*3 in only 1 h and increasing ω_{M0} = 30 wt% the time $t_{1/2}$ is extended to 1.6 h.

Table S1. Kinetic rate coefficients estimated by a *pseudo*-first order reaction.

ω_{M0} (wt.%)	$[DEAEMA]_0$ M	T (°C)	k_{obs} (s^{-1})	k_{tran} (L mol^{-1} s^{-1})	R^2	$t_{1/2}$ (h)
10	0.44	26.80	1.86×10^{-5}	8.36×10^{-7}	1.00	10.35
		43.50	4.42×10^{-5}	2.00×10^{-6}	0.99	4.35
		60.00	1.10×10^{-4}	4.94×10^{-6}	0.99	1.75
		70.00	1.89×10^{-4}	8.50×10^{-6}	1.00	1.02
30	1.31	26.80	1.30×10^{-5}	7.40×10^{-7}	1.00	14.82
		43.50	3.55×10^{-5}	2.02×10^{-6}	0.99	5.42
		60.00	7.14×10^{-5}	4.05×10^{-6}	0.99	2.70
		70.00	1.15×10^{-4}	6.53×10^{-6}	0.99	1.67
60	2.85	26.80	2.3×10^{-6}	2.29×10^{-7}	1.00	83.72

		43.50	5.62×10^{-6}	5.77×10^{-7}	0.99	34.27
		70.00	1.50×10^{-5}	1.53×10^{-6}	0.99	12.83

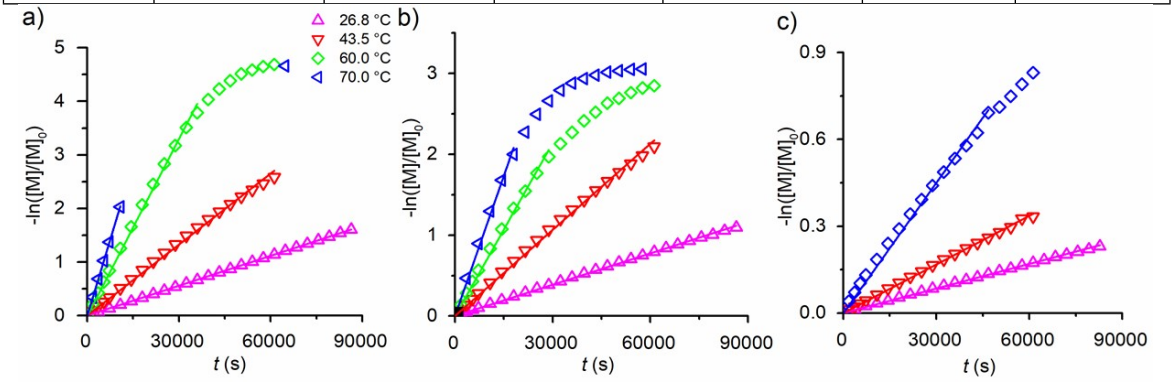

Figure S7. *Pseudo*-first-order kinetic plots for the transesterification analyzed with **Eqn. S1**, varying the temperature (labels) and ω_{M0}: a) 10 wt%, b) 30 wt% and c) 60 wt%. Symbols are the experimental data and lines are regressions with the estimated values shown in **Table S2**.

S.6. Validation of *pseudo*-first-order reaction, experimental data *versus* model.

In **Figure S8** is the comparison between the experimental data and the predicted curves obtained by a *pseudo*-first-order reaction. Data are well described by the model for experiments with an excess of CD_3OD, also for that experiment with ω_{M0} = 60 wt%, but the last points of the latter present considerable discrepancies.

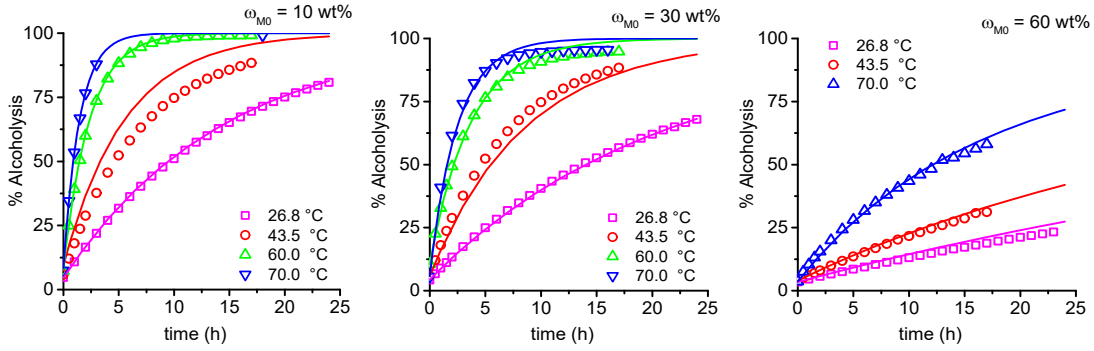

Figure S8. Evolution of the alcoholysis degree (D_A, mol%) in time and the variation of the reaction temperature (labels). The value of ω_{M0} was varying at: a) 10, b) 30, and c) 60 wt%. Symbols are the experimental data obtained via ^{1}H-NRM *in situ* measurements and lines

represent a model prediction with a *pseudo*-first-order kinetic equation and using Equations (X6-8).

S.7. Estimation of the Arrhenius parameters A and E_a as a function of $[DEAEMA]_0$ or ω_{M0}.

A and E_a as a function of $[DEAEMA]_0$

The values of ln(A) and E_A from **Table 2** of the main report, were used to know their dependency on the initial concentration of DEAEMA, $[DEAEMA]_0$. The preexponential factor, A, is linearly dependent on [DEAEMA]0 as shown in **Figure S9** $[DEAEMA]_0$, **Equation S3** obtained by a linear regression in Origin software (), resulting in a value of R^2 = 0.9997.

$$A\left(L\,mol^{-1}s^{-1}\right) = -5.9726\,(\pm 0.6141) + 1.6688\,(\pm 0.0205)[DEAEMA]_0 \quad \text{(S3)}$$

Also, E_A is described by **Equation X8** with a second-order polynomial expression as shown in Figure Xb and using the dependent variable in logarithmic base.

$$E_A\left(kJ\,mol^{-1}\right) = 22.0200 + 25.4789\ln[DEAEMA]_0 - 6.8067\ln[DEAEMA]_0^2 \quad \text{(S4)}$$

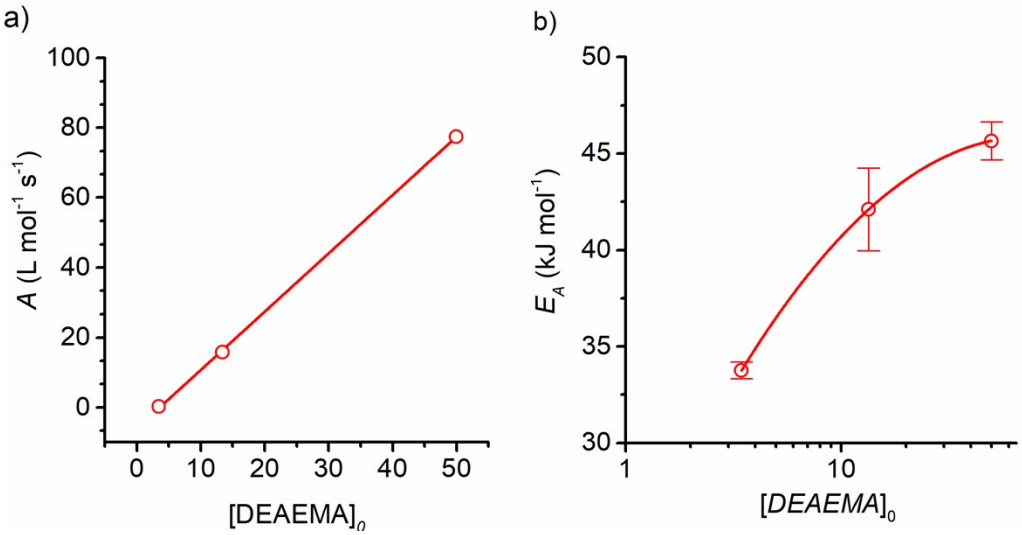

Figure S9. Best fit Arrhenius parameters (a) ln (A) and (b) E_A values (data, see Table X3) determined for DEAEMA transesterification as a function of $[DEAEMA]_0$ Lines show fits summarized by **Equation S3 and S4**.

***A* and E_a as a function of** ω_{M0}

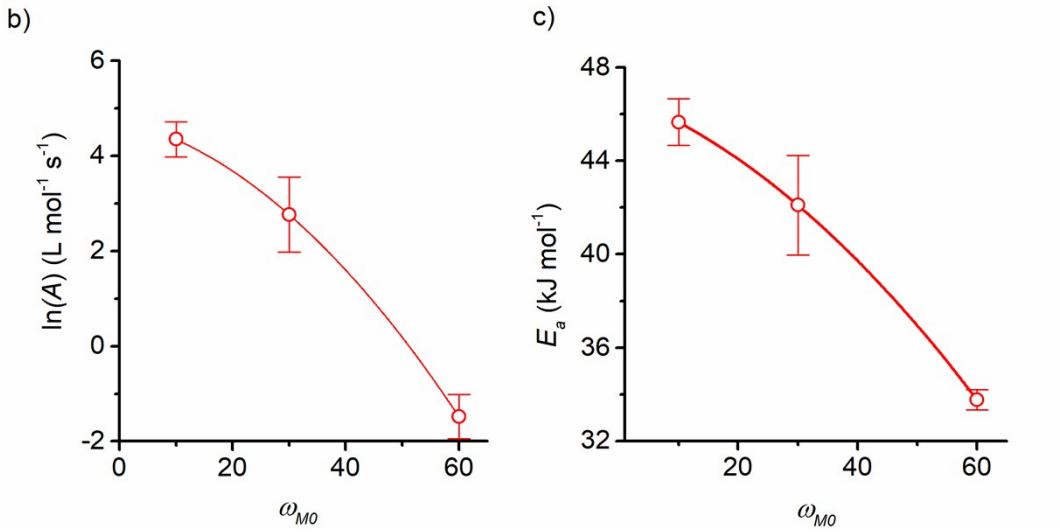

Figure S10. Best fit Arrhenius parameters (a) ln (A) and (b) E_A values (data, see Table X3) determined for DEAEMA transesterification as a function of ω_{M0}. Lines show quadratic fits summarized by **Equations 5 and 6** of the article.

S.8. Calculations of transesterification, conversion, remaining monomer composition and copolymer composition.

i. Alkanolamine moles:

$$Am\ (moles) = \frac{\int H_{7,6^*,7^*,g} - 2\int H_5 - 2\int H_e}{6} \quad \text{(S5)}$$

ii. PMMA moles:

$$PMMA\ (moles) = \frac{\int H_{5^*+9^*} - 2\ Am}{2}$$

(S6)

iii. Degree of alcoholysis

$$D_a\ (mol\ \%) = \frac{2\ Am}{\int H_{5^*} + \int H_5 + 2\ Am} \times 100$$

(S7)

iv. DEAEMA conversion

$$X_{DEAEMA}(mol\ \%) = \frac{\int H_5}{\int H_{5^*} + \int H_5 + 2\ Am} \times 100$$

(S8)

v. % of remaining DEAEMA monomer in the reaction mixture

$$X_{DEAEMA}(mol\ \%) = \frac{\int H_{5^*}}{\int H_{5^*} + \int H_5 + 2\ Am} \times 100$$

(S9)

vi. Remaining DEAEMA composition in the reaction mixture, f_{DEAEMA}

$$f_{DEAEMA}(mol\ \%) = \frac{\frac{\int H_5}{2}}{\frac{\int H_5}{2} + \frac{\int H_9}{3}}$$

(S10)

vii. Remaining MMA composition in the reaction mixture, f_{MMA}

$$f_{MMA}(mol\ \%) = 1 - f_{DEAEMA}$$

(S11)

viii. Cumulative copolymer composition of DEAEMA

$$F_{DEAEMA}(mol\ \%) = \frac{\int H_e}{\int H_e + 2PMMA} \quad \text{(S12)}$$

ix. Cumulative copolymer composition of MMA

$$F_{MMA}(mol\ \%) = 1 - F_{DEAEMA} \quad \text{(S13)}$$

S.9. NMR spectroscopy and DCS of copolymers and

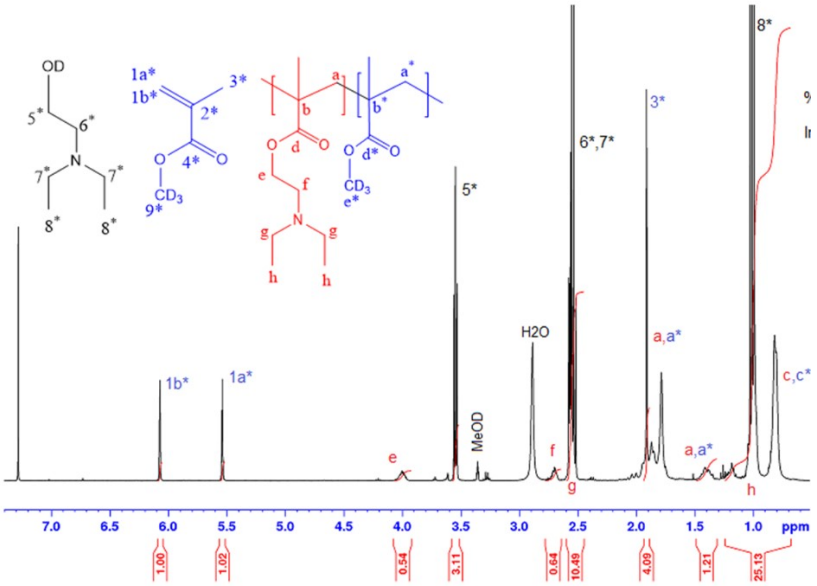

Figure S11. ^{1}H-NMR (400 MHz, CD_3Cl, r.t.) spectra of the precipitated polymer with a resulting copolymer composition of (DEAEMA: MMA-d_3) = 5:95 mol%. Initial conditions of the reaction: initial ratio ω_{M0} = 10 wt% and molar ratio DEAEMA: AIBN = 92:1 in CD_3OD at 70°C, and a total time reaction of 17 h.

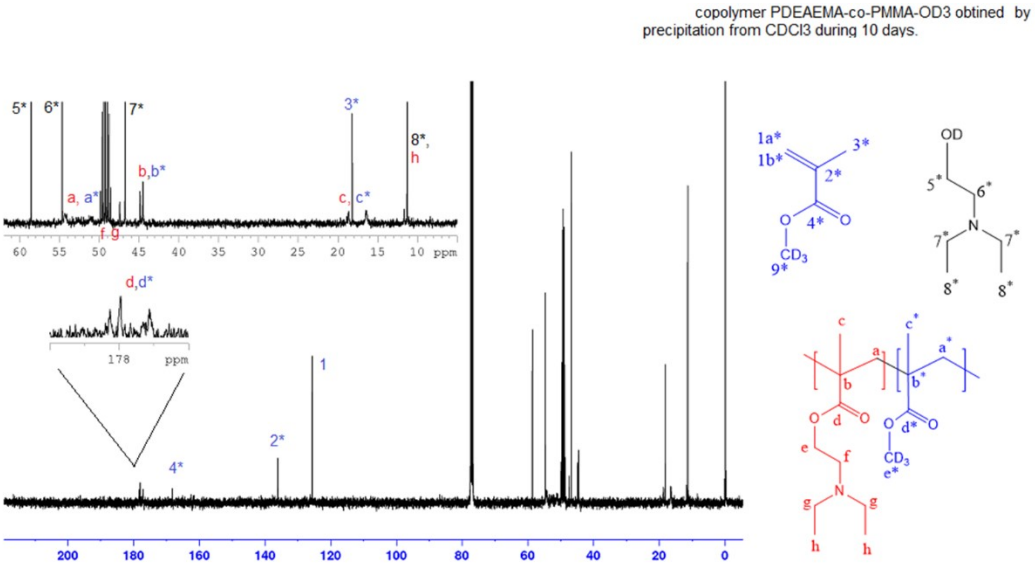

Figure S12. $^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$, r.t) spectrum of copolymer PDEAEMA-co-PMMAOD$_3$, % molar composition 5:95 obtained by ^{1}H-NMR after it was precipitate from CD_3OD. Initial conditions of the reaction: 1:46 (DEAEMA: CD_3OD) initial molar ratio, ω_{M0} = 10 wt% and molar ratio DEAEMA: AIBN = 92:1 in CD_3OD at 70°C, and a total time reaction of 17 h.

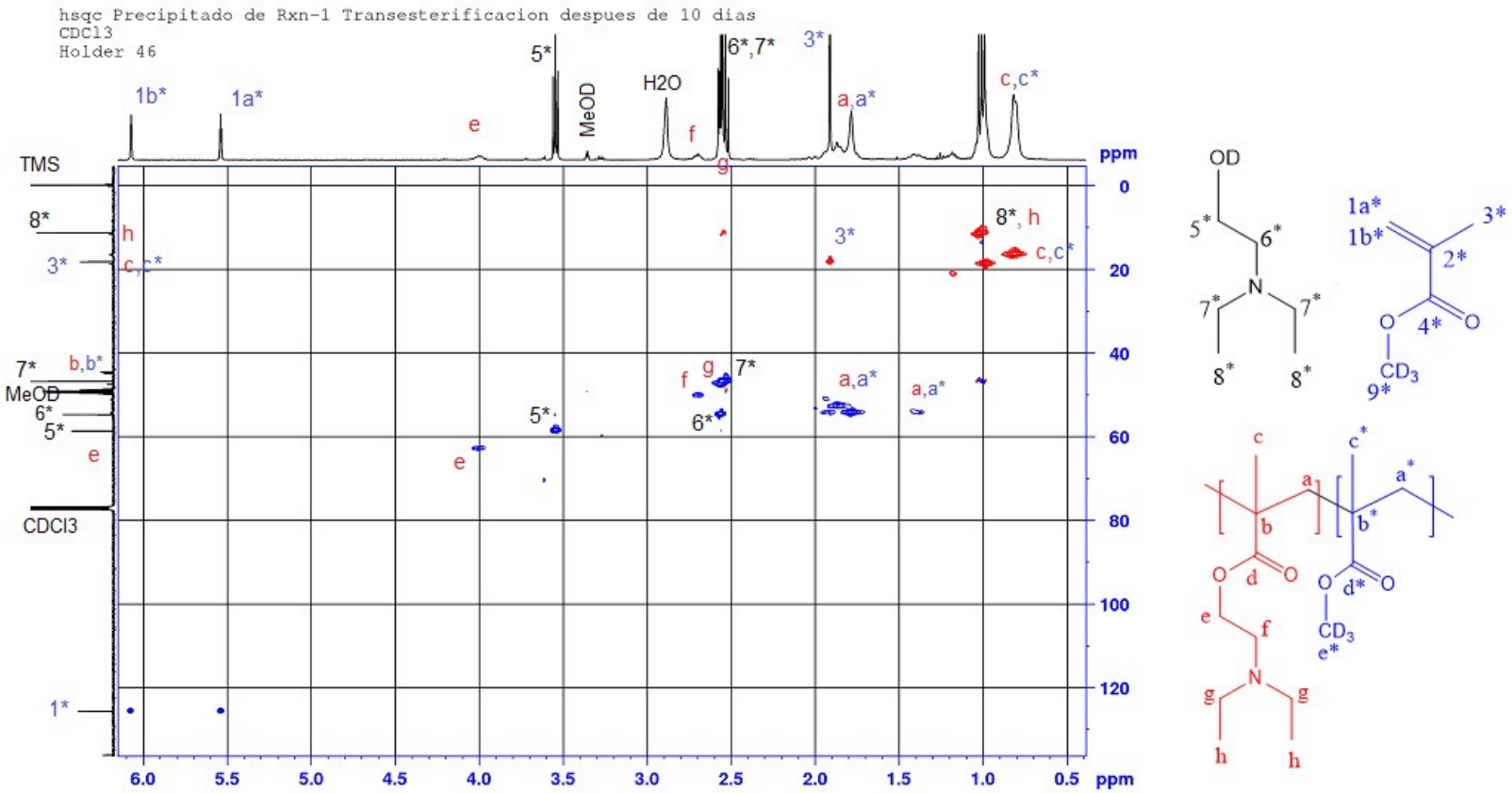

Figure S13. Edited HSQC (400MHz, $CDCl_3$, r.t.) of copolymer PDEAEMA-coPMMAOD$_3$, after it was precipitate from CD_3OD. Initial conditions of the reaction: initial molar ratio of DEAEMA: CD_3OD = 1:46, ω_{M0} = 10 wt% and molar ratio DEAEMA: AIBN = 92:1 in CD_3OD at 70°C, and a total time reaction of 17 h.

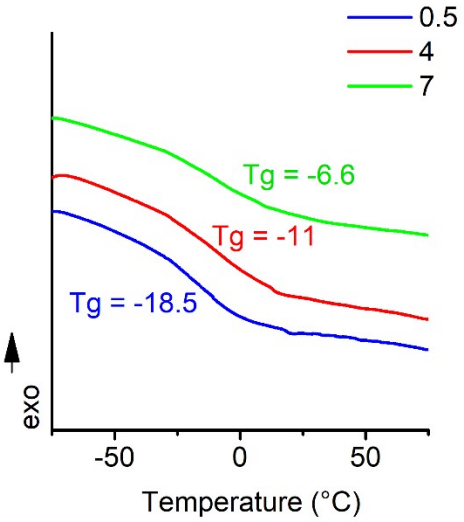

Figure S14. Stacked DSC thermograms for experiment with a mixture of methanol/ CDCl3 at 60 °C, DEAEMA: AIBN molar ratio of 92: 1 and DEAEMA: methanol molar ratio of 1:8. Labels indicate the time reaction (hours).

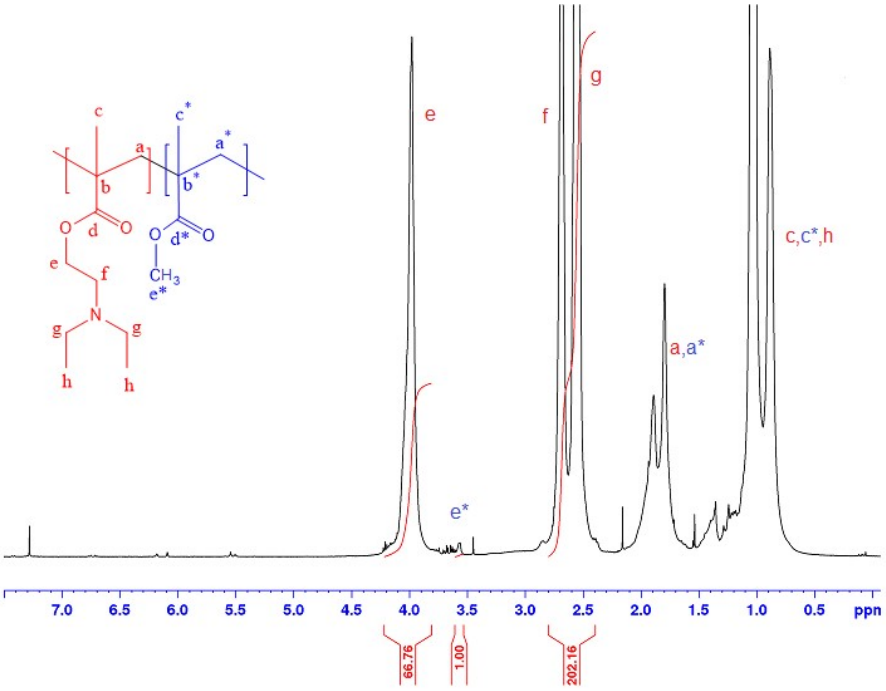

Figure S15. [1]H-NMR (400 MHz, CDCl3, r.t) spectrum of copolymer poly(DEAEMA-co-MMA-d_3), after it was lyophilized twice at the end of the kinetic. Initial conditions of the

reaction: initial molar ratio of DEAEMA: CH_3OH = 1:1, ω_{M0} = 58 wt% and molar ratio DEAEMA: AIBN = 92:1 in $CDCl_3$ at 70°C, and a total time reaction of 17 h.

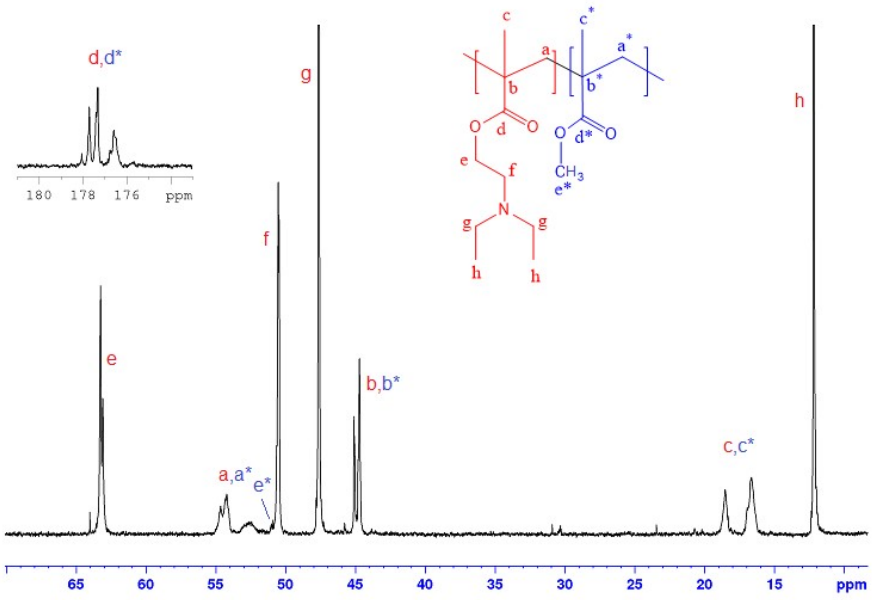

Figure S16. $^{13}C\{1H\}$-NMR (100 MHz, CDCl3, r.t) spectrum of copolymer poly(DEAEMA-co-MMA-d_3), % molar composition 99:1 obtained by 1H-NMR after it was lyophilized at the end of kinetic. Initial conditions of the reaction: initial molar ratio of DEAEMA: CH_3OH = 1: 1, ω_{M0} = 58 wt% and molar ratio DEAEMA: AIBN = 92:1 in $CDCl_3$ at 70°C, and a total time reaction of 17 h.

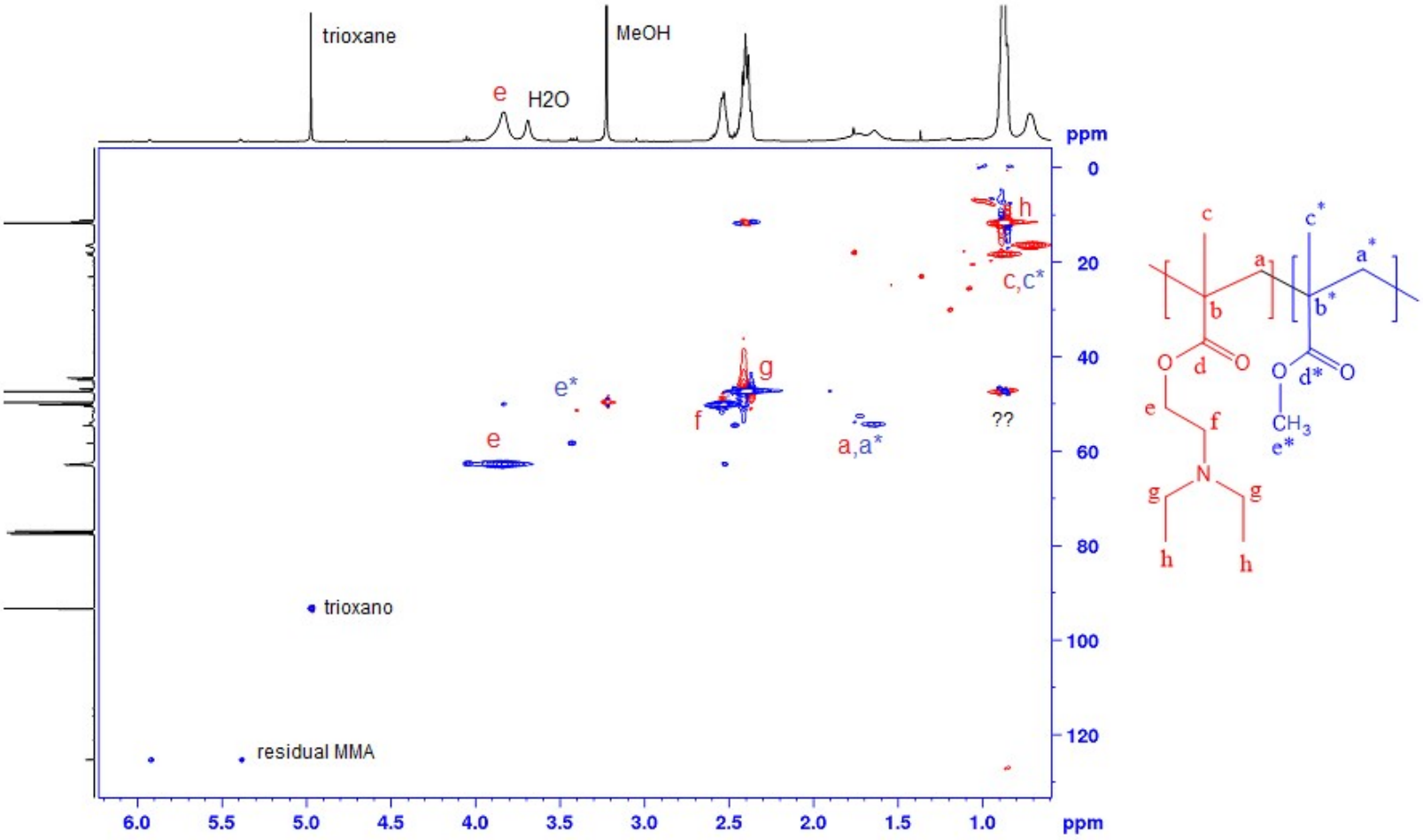

Figure S17. Edited HSQC (400MHz, $CDCl_3$, r.t.) of copolymer PDEAEMA-coPMMAOD$_3$, after purified. Initial conditions of the reaction: 1:1 (DEAEMA: CD_3OD) molar ratio, ω_{M0} = 58 wt% and 92:1 (DEAEMA: AIBN) molar ratio in CD_3OD at 70°C and a total time reaction of 17 h.

S.10. Precipitated polymer

Figure S18. Picture of the precipitated polymer with a resulting copolymer composition of (DEAEMA: MMA-d3) = 96: 4 mol%. Initial conditions of the reaction: initial ratio ω_{M0} = 10 wt% and molar ratio DEAEMA: AIBN = 92: 1 in CD_3OD at 70°C, and a total time reaction of 17 h.