

Supporting Information

Vitrimerization of Crosslinked Poly (Ethylene-Vinyl Acetate): The effect of Catalyst

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Keywords: Vitrimerization, Crosslinked Poly (Ethylene- Vinyl Acetate), EVA, Recycling,
Transesterification, Vitrimer

Table S1. Properties of EVA material selected for vitrimerization.

Sample	wt% VA (¹ H-NMR) ¹	nominal MFR ^a (190 °C)	Mw ^b (g/mol) ¹	[VA]/ [DCP] (mol/mol)
EVA	21.8	2.1	103,591	35 ± 0.03

^a melt flow rate from the datasheet

^b molecular weight of initial thermoplastic EVAs

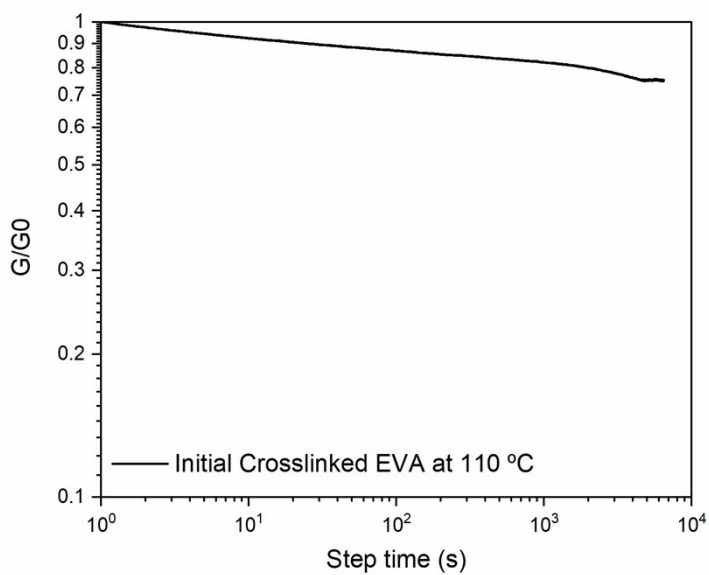


Figure S1. Stress relaxation test of crosslinked EVA at 110°C showing no relaxation, indicative of a highly crosslinked network.

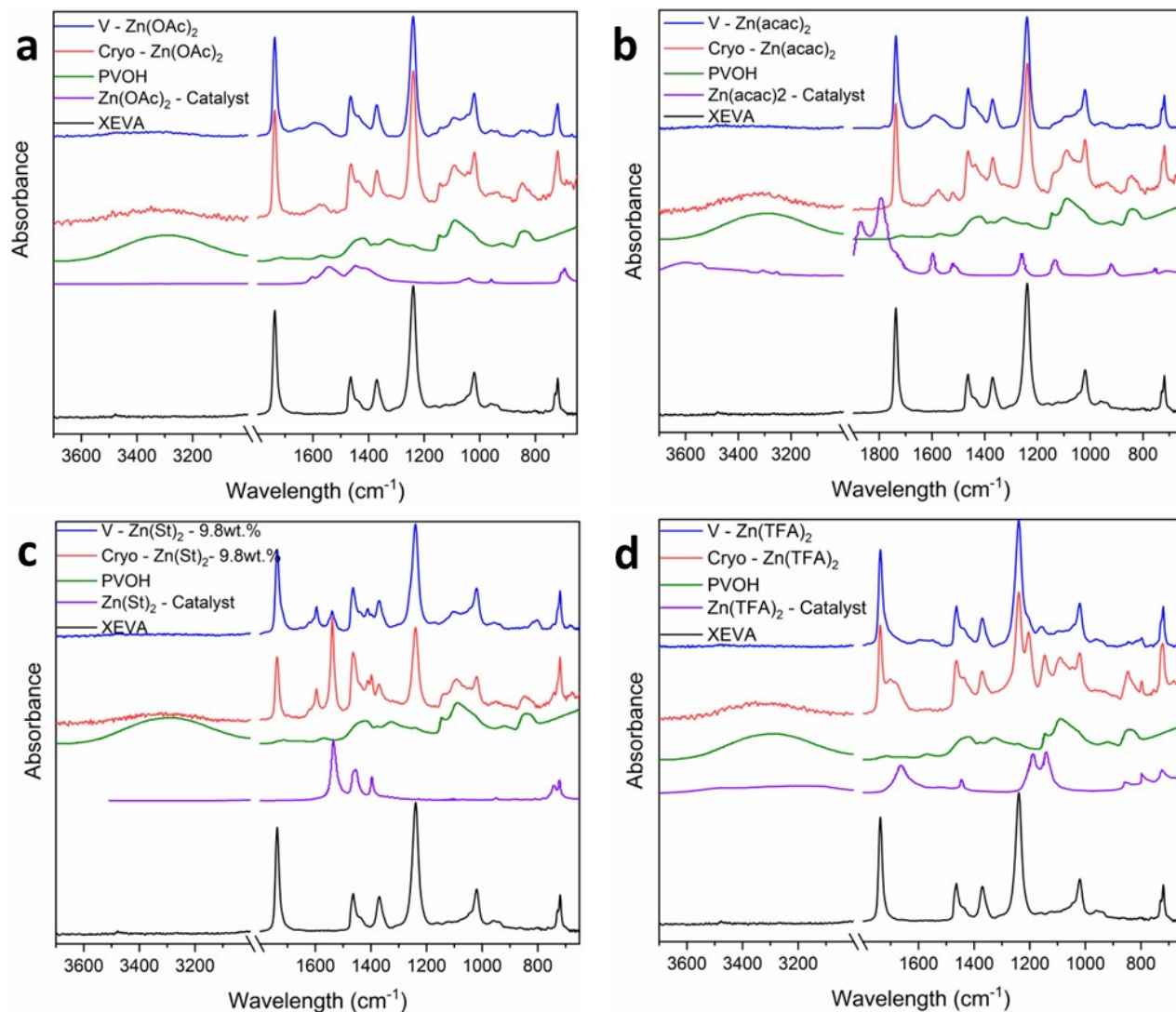
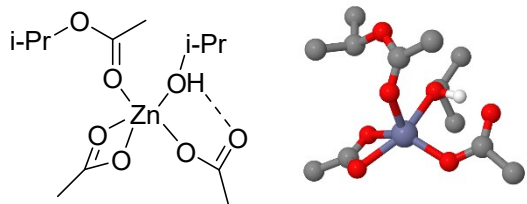


Figure S2. FTIR spectra of initial crosslinked and vitrimerized EVAs along with FTIR spectra of PVOH, zinc salt and cryo-milled samples before compression molding.

Table S2. Cartesian coordinates of optimized geometries in angstrom, alkyl hydrogens are hidden on the figure for clarity.

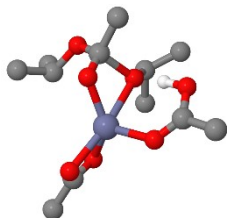
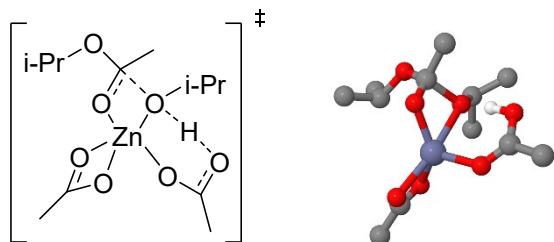
A1. $\text{Zn}(\text{OAc})_2$ catalyzed reactant complex



Zn	-0.409551	0.816426	0.300812
O	-2.265752	0.826566	0.889729

C	-3.028427	-0.192855	0.890883
O	-2.745911	-1.303486	0.401675
C	-4.369541	0.006872	1.543234
O	0.837998	1.725001	-1.146239
C	1.026288	2.663489	-0.318787
O	0.459483	2.635299	0.803796
C	1.950682	3.790297	-0.665261
C	3.689443	-0.389730	0.884655
O	0.632812	-0.397123	1.632663
C	2.675282	-1.081844	0.005014
O	1.906323	-2.031169	0.797848
C	3.290479	-1.889001	-1.109433
C	0.910560	-1.583644	1.519542
C	0.131924	-2.653265	2.201751
O	-0.591726	-0.920846	-0.870996
C	-0.624188	-0.906039	-2.298683
C	-1.733673	-0.007770	-2.805956
C	-0.744846	-2.326837	-2.808764
H	-4.897084	0.817636	1.037107
H	-4.224148	0.318843	2.579090
H	-4.960643	-0.905220	1.504537
H	2.959565	3.516159	-0.344930
H	1.663713	4.697044	-0.135918
H	1.969571	3.955463	-1.741115
H	4.277637	0.303500	0.279900
H	3.199531	0.180223	1.674190
H	4.370825	-1.116224	1.333713
H	0.006816	-2.387886	3.251757
H	2.518222	-2.387454	-1.696879
H	3.851480	-1.226726	-1.771065
H	1.975731	-0.353162	-0.406093
H	-0.863469	-2.669859	1.747960
H	3.973440	-2.644526	-0.714677
H	0.603598	-3.627482	2.101522
H	0.338429	-0.483810	-2.600098
H	-2.708302	-0.373908	-2.472077
H	-1.702509	-2.761113	-2.508401
H	-1.734146	0.019451	-3.897913
H	-0.686363	-2.352136	-3.899185
H	-1.597195	1.012985	-2.443528
H	0.055032	-2.949893	-2.403861
H	-1.482394	-1.210092	-0.477321

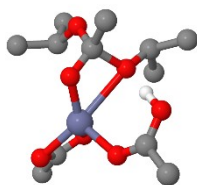
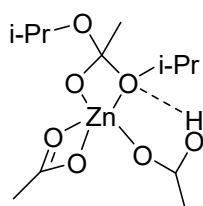
A2. Zn(OAc)₂ catalyzed transition state



Zn	-0.124839	1.030500	-0.324045
O	1.822745	0.524877	-0.362157
O	2.715139	2.562541	-0.546817
C	2.794622	1.291518	-0.360693
C	4.168494	0.764717	-0.113268
H	4.889203	1.261094	-0.762031
H	4.190016	-0.313188	-0.251930
H	4.439657	0.995290	0.920402
O	-1.283724	0.337788	-1.873336
O	-1.128282	-0.771335	0.003447
C	-1.597808	-0.662012	-1.156897
C	-2.546029	-1.684929	-1.698975
H	-2.312291	-1.896092	-2.742163
H	-3.557000	-1.271018	-1.666086
H	-2.516740	-2.594375	-1.103234
O	0.366449	3.185250	-1.018545
H	1.712778	2.869584	-0.742852
O	-0.432211	2.394871	1.011501
C	-0.435281	3.561494	0.467003
C	0.424245	4.629614	1.086411
H	1.442192	4.265192	1.210069
H	0.009725	4.858833	2.069993
H	0.418622	5.538244	0.485733
O	-1.612227	4.114369	0.080254
C	0.179137	4.011549	-2.166902
C	1.418621	4.841880	-2.447147
C	-0.206333	3.146962	-3.348966
H	-0.651566	4.683935	-1.927779
H	1.705137	5.433438	-1.575663
H	1.230440	5.528086	-3.275856
H	2.263951	4.205694	-2.721664
H	-1.091061	2.548648	-3.129787
H	0.605442	2.458690	-3.600372
H	-0.407352	3.768403	-4.225066
C	-2.697076	3.244216	-0.279731

C	-3.467876	2.823396	0.952984
C	-3.551633	4.015251	-1.259641
H	-2.291376	2.361868	-0.784796
H	-2.823066	2.285018	1.645555
H	-4.298991	2.173376	0.669144
H	-3.876722	3.702634	1.457448
H	-2.985737	4.280431	-2.154075
H	-3.923897	4.933425	-0.799212
H	-4.408100	3.410324	-1.563519

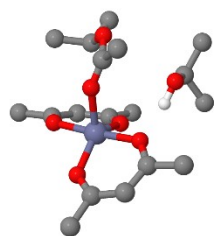
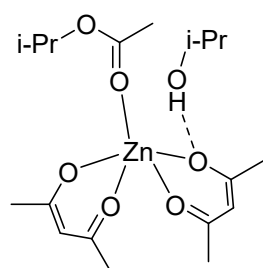
A3. Zn(OAc)₂ catalyzed tetrahedral intermediate



Zn	-0.655032	0.889778	0.307368
O	-2.517496	0.086732	0.318377
C	-2.849996	-1.091527	0.460507
O	-2.034032	-2.093723	0.402864
C	-4.269003	-1.459845	0.733007
O	-0.281296	1.722172	-1.547487
C	-0.564551	2.847626	-1.043310
O	-0.899375	2.923552	0.170941
C	-0.470911	4.086770	-1.875635
C	2.972417	1.610121	1.163207
O	0.381463	-0.004344	1.608573
C	2.671390	0.542120	0.131127
O	2.408279	-0.710987	0.764543
C	3.837098	0.316052	-0.807080
C	1.100745	-1.002662	1.127219
C	1.170220	-2.205518	2.042579
O	0.349017	-1.398589	-0.143180
C	0.993604	-2.208211	-1.138803
C	0.793745	-1.538532	-2.481147
C	0.449417	-3.623399	-1.116367
H	-4.920855	-0.611056	0.544662
H	-4.351421	-1.752524	1.782883

H	-4.559105	-2.319710	0.129612
H	0.541761	4.487097	-1.778268
H	-1.168507	4.841390	-1.517032
H	-0.646524	3.857766	-2.925116
H	3.173302	2.565637	0.671918
H	2.133185	1.733009	1.845820
H	3.855789	1.328734	1.742312
H	1.629727	-1.890688	2.979246
H	3.594315	-0.428276	-1.567520
H	4.103155	1.247554	-1.311007
H	1.800334	0.837731	-0.465155
H	0.164926	-2.572924	2.247105
H	4.707911	-0.034173	-0.247662
H	1.775985	-3.000177	1.606238
H	2.056954	-2.218688	-0.888138
H	-0.268778	-1.501494	-2.735906
H	-0.610686	-3.640636	-1.381737
H	1.312328	-2.095175	-3.265155
H	0.986723	-4.239228	-1.840972
H	1.167054	-0.514156	-2.468967
H	0.564649	-4.079546	-0.132092
H	-1.064438	-1.805249	0.205160

B1. Zn(acac)₂ catalyzed attacking complex

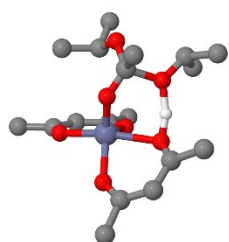
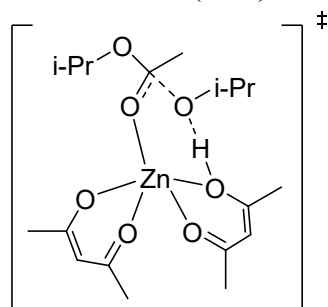


C	-1.962831	0.361620	2.929349
H	-2.299913	-0.672661	2.819465
H	-2.812163	0.993020	3.186241
H	-1.236486	0.373797	3.744971
C	-1.283440	0.788844	1.660233
C	-1.809653	1.861912	0.936766
H	-2.679783	2.358867	1.342746
C	-1.280235	2.360395	-0.266329
C	-1.944076	3.546708	-0.907118
H	-2.182958	3.306935	-1.945440

H	-1.233283	4.376558	-0.926895
H	-2.846988	3.859610	-0.384349
O	-0.267227	0.107850	1.336655
O	-0.281398	1.900002	-0.874517
C	4.793705	2.150147	-0.670036
H	4.628221	3.018671	-0.028242
H	5.809714	1.783739	-0.530805
H	4.663902	2.485656	-1.701542
C	3.753636	1.111856	-0.361204
C	4.174141	-0.157611	0.061696
H	5.238268	-0.329166	0.142609
C	3.325262	-1.214130	0.392458
C	3.915966	-2.517549	0.843698
H	3.597131	-2.714952	1.870620
H	3.518964	-3.328680	0.228892
H	5.003751	-2.520792	0.798356
O	2.558459	1.482997	-0.512442
O	2.060064	-1.167790	0.354141
Zn	0.915133	0.409723	-0.244716
H	1.042085	-2.612856	0.413514
H	-0.687734	-3.199816	3.461914
H	0.745424	-4.071573	2.881668
H	-2.195590	-4.608159	1.876976
C	0.083393	-3.223178	2.686910
H	-0.756842	-5.486576	1.324636
C	-1.373078	-4.599209	1.157912
H	0.659992	-2.298150	2.756554
C	-0.536348	-3.348863	1.308057
H	-1.790304	-4.659728	0.150246
H	-1.179103	-2.469386	1.148538
O	0.456793	-3.387210	0.303475
H	-3.219628	-2.493794	-0.113502
C	-3.539619	-1.712624	-0.804019
H	-4.145994	-0.990970	-0.253307
H	-1.732945	-0.575636	-0.621753
C	-2.351284	-1.008021	-1.408110
C	-0.275153	-1.837853	-2.224337
O	-1.567076	-2.033230	-2.070094
H	-0.248193	-3.468502	-3.609913
H	-4.160050	-2.165831	-1.580476
C	0.404908	-2.985485	-2.884965
H	0.637618	-3.699817	-2.090073
O	0.309386	-0.831490	-1.864839

C	-2.730646	0.054252	-2.412648
H	-3.353838	0.806677	-1.925423
H	1.329191	-2.648086	-3.348293
H	-1.844305	0.551850	-2.806371
H	-3.299171	-0.385151	-3.235741

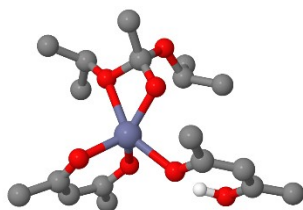
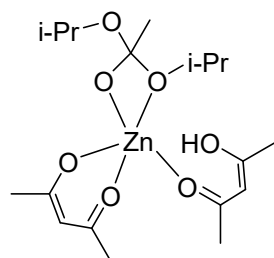
B2. Zn(acac)₂ catalyzed transition state



C	-2.015913	1.028935	2.984438
H	-2.462243	0.031074	2.968011
H	-2.789352	1.765470	3.197036
H	-1.274618	1.034022	3.786650
C	-1.322548	1.275298	1.675049
C	-1.754422	2.334891	0.873842
H	-2.574076	2.933101	1.246836
C	-1.201680	2.705463	-0.364463
C	-1.787991	3.883955	-1.088462
H	-2.163876	3.547791	-2.058064
H	-0.995731	4.609324	-1.286229
H	-2.593014	4.364012	-0.533878
O	-0.386303	0.467104	1.403922
O	-0.244643	2.133210	-0.945478
C	4.771612	1.836420	-0.443930
H	4.478175	2.848018	-0.167466
H	5.694032	1.552243	0.062694
H	4.959539	1.824390	-1.522309
C	3.645807	0.887751	-0.148932

C	3.988226	-0.473341	0.106569
H	5.027955	-0.749619	-0.003222
C	3.099262	-1.462503	0.424015
C	3.512890	-2.892431	0.500060
H	3.313921	-3.282739	1.501621
H	2.911065	-3.478692	-0.199883
H	4.566774	-3.022903	0.262907
O	2.492913	1.350112	-0.196651
O	1.854465	-1.201312	0.700722
Zn	0.662516	0.484818	-0.278117
H	1.119533	-1.956681	0.403440
H	-1.728809	-3.918232	2.249263
H	-0.223919	-3.003183	2.436573
H	-0.436400	-5.738052	0.894660
C	-1.082095	-3.172681	1.780444
H	1.043885	-4.806576	1.143826
C	0.176369	-4.929098	0.489646
H	-1.625742	-2.230985	1.698955
C	-0.624865	-3.643055	0.413718
H	0.528146	-5.229388	-0.498836
H	-1.498241	-3.795046	-0.226226
O	0.144531	-2.613910	-0.190896
H	-3.467670	-2.294933	0.127480
C	-3.650334	-1.564316	-0.662487
H	-4.278610	-0.768201	-0.256781
H	-1.805081	-0.535199	-0.356810
C	-2.353852	-0.986664	-1.187509
C	-0.212759	-2.015180	-1.616430
O	-1.593919	-2.076218	-1.710977
H	-0.148486	-3.987176	-2.506125
H	-4.199091	-2.059172	-1.467665
C	0.337552	-3.016468	-2.609332
H	1.411889	-3.119912	-2.460872
O	0.349784	-0.848273	-1.653463
C	-2.591461	0.047946	-2.267944
H	-3.191532	0.872423	-1.874460
H	0.152689	-2.635968	-3.614390
H	-1.645014	0.446038	-2.630402
H	-3.131516	-0.405955	-3.103136

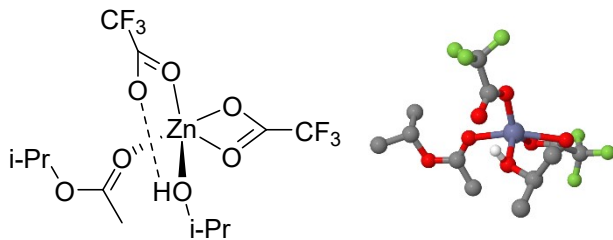
B3. Zn(acac)₂ catalyzed tetrahedral intermediate



C	-3.324963	-3.512911	0.693381
H	-2.784467	-4.272077	1.263608
H	-3.927908	-3.995982	-0.073806
H	-3.978463	-2.990235	1.395929
C	-2.337663	-2.534280	0.126937
C	-2.297642	-2.349874	-1.261838
H	-2.995335	-2.930001	-1.849505
C	-1.425378	-1.508807	-1.966548
C	-1.524268	-1.459324	-3.463219
H	-2.239435	-2.176053	-3.863727
H	-0.537330	-1.643425	-3.892974
H	-1.820604	-0.449783	-3.760529
O	-1.611208	-1.950498	0.981622
O	-0.542988	-0.760453	-1.459179
C	2.292034	-1.270980	2.632268
H	1.746683	-0.339176	2.821925
H	1.644817	-2.097101	2.932964
H	3.216405	-1.285759	3.207270
C	2.534033	-1.335069	1.166295
C	3.834293	-1.138046	0.637320
H	4.669051	-0.988715	1.305586
C	4.038533	-1.070126	-0.719074
C	5.359448	-0.793259	-1.333286
H	5.300439	0.134607	-1.908194
H	6.140061	-0.703000	-0.580924
H	5.613578	-1.592084	-2.033960
O	1.558958	-1.534518	0.393221
O	3.067846	-1.229667	-1.579154
Zn	-0.348473	-0.538893	0.497480
O	0.399137	0.905461	1.503139
C	-0.438380	1.936648	1.364324
O	0.043652	2.981893	0.557461
C	0.680926	2.612028	-0.660084
C	2.177928	2.463024	-0.461500
H	0.267378	1.660676	-1.013061
C	0.353536	3.689668	-1.672169

O	-1.603538	1.332580	0.712471
C	-2.680511	2.142640	0.258890
C	-3.021805	1.721595	-1.156076
C	-3.869184	1.993139	1.188998
H	-2.333875	3.181476	0.251875
C	-0.830182	2.582549	2.677671
H	0.074956	2.946108	3.163873
H	-1.504105	3.426901	2.525091
H	-1.307000	1.837890	3.314346
H	2.236235	-1.389684	-1.035928
H	-4.192964	0.949396	1.214157
H	-4.706785	2.605374	0.845191
H	-3.616759	2.296528	2.205459
H	-3.346998	0.677520	-1.170097
H	-2.152508	1.815911	-1.808239
H	-3.830323	2.337714	-1.556465
H	2.610223	3.414884	-0.140785
H	2.657348	2.162669	-1.397720
H	2.381564	1.713049	0.301068
H	0.823838	3.468799	-2.633301
H	0.720938	4.658051	-1.322989
H	-0.724422	3.769616	-1.824042

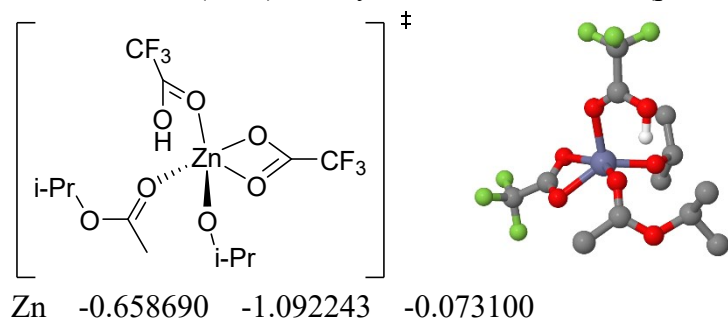
C1. Zn(TFA)₂ catalyzed reactant complex



O	-1.998390	-1.773058	0.413950
O	-2.238466	0.089532	-0.739541
C	-2.676646	-0.994098	-0.255603
C	-4.164169	-1.293281	-0.527750
F	-4.423350	-1.251635	-1.833572
F	-4.523322	-2.483052	-0.069338
F	-4.922783	-0.369673	0.075333
O	1.234723	-0.988935	-0.631694
O	2.457351	-0.236972	1.099725
C	2.304283	-0.778111	0.007220
C	3.572808	-1.245343	-0.749149
F	3.396153	-2.433289	-1.321045

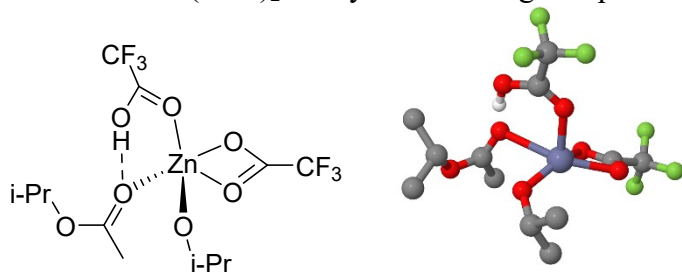
F	3.856141	-0.359192	-1.715308
F	4.627135	-1.324712	0.052648
Zn	-0.391219	-0.131664	0.016561
O	0.038359	0.156701	1.990535
C	-0.202968	2.868372	-0.102796
C	-1.466472	3.020761	0.668039
H	-1.739061	4.065823	0.788051
H	-2.257560	2.466566	0.159502
H	-1.319161	2.557236	1.646854
O	0.396581	3.996131	-0.382545
C	1.663405	3.940953	-1.107089
C	1.384302	3.809939	-2.585237
C	2.399261	5.203679	-0.738728
H	2.197889	3.060426	-0.745653
O	0.259705	1.786811	-0.443901
H	1.027890	0.073395	1.882017
C	-0.420129	-0.702213	3.057170
C	0.194130	-2.079044	2.939280
C	-0.122201	-0.032553	4.379720
H	-1.500219	-0.774866	2.910482
H	0.956903	0.062260	4.528261
H	-0.526668	-0.624320	5.203512
H	-0.566378	0.963558	4.420371
H	-0.053318	-2.534129	1.979589
H	-0.191230	-2.726870	3.729088
H	1.281393	-2.027634	3.041508
H	3.375593	5.210840	-1.226252
H	2.553974	5.266918	0.339236
H	1.844477	6.085598	-1.065816
H	2.328776	3.780909	-3.131792
H	0.805827	4.664446	-2.943426
H	0.840371	2.890992	-2.803887

C2. Zn(TFA)₂ catalyzed transition state 1 (proton transfer)



O	-1.878339	-2.836807	0.382064
O	-2.589760	-1.089885	-0.744696
C	-2.766329	-2.223637	-0.225493
C	-4.172401	-2.835900	-0.366728
F	-4.514588	-2.912989	-1.653562
F	-4.240044	-4.050753	0.155380
F	-5.066649	-2.062745	0.254568
O	0.738642	-2.093670	-1.320991
O	2.216865	-0.399914	-1.390373
C	1.834511	-1.623509	-1.544534
C	2.977297	-2.516869	-2.074271
F	3.982972	-2.521421	-1.202737
F	2.558153	-3.754717	-2.250656
F	3.424660	-2.043461	-3.234878
C	1.587646	-1.938182	2.222984
H	0.963605	-2.723459	1.781033
H	1.919808	-2.290392	3.203257
H	2.470861	-1.801091	1.594150
C	0.804185	-0.639403	2.329045
H	1.460767	0.113260	2.795049
O	0.454151	-0.147832	1.064789
H	1.451419	0.153840	-1.088238
C	-0.418704	-0.804500	3.215851
H	-0.976006	0.133378	3.268301
H	-0.144394	-1.101786	4.231712
H	-1.080237	-1.577532	2.808394
C	-2.183092	1.830689	-2.216552
H	-1.990411	1.675380	-3.279894
H	-2.818105	1.008781	-1.880307
H	-2.672342	2.788451	-2.060152
C	-0.888869	1.747803	-1.485218
O	-0.195756	0.734686	-1.495210
O	-0.569239	2.840703	-0.845935
C	0.649408	2.855298	-0.036905
H	0.764200	1.852056	0.384147
C	1.815170	3.229770	-0.921595
H	2.733684	3.233899	-0.331590
H	1.675094	4.226822	-1.345795
H	1.945858	2.519935	-1.740125
C	0.391656	3.848863	1.066740
H	1.263381	3.895351	1.722027
H	-0.468096	3.546033	1.665822
H	0.208058	4.847697	0.664219

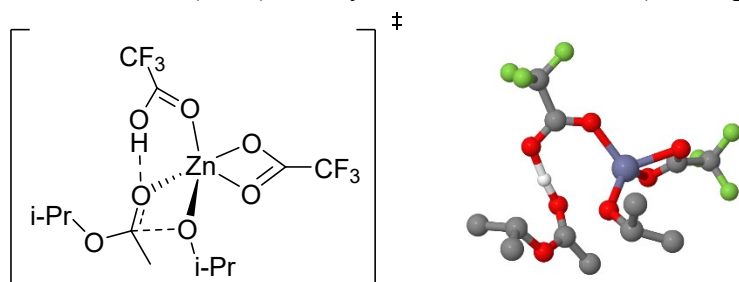
C3. Zn(TFA)₂ catalyzed attacking complex



Zn	-0.639028	-1.264188	-0.047873
O	-1.642921	-3.085790	0.446788
O	-2.408092	-1.654182	-1.035003
C	-2.497290	-2.720798	-0.379637
C	-3.746583	-3.588098	-0.622525
F	-3.867815	-3.873975	-1.918604
F	-3.700719	-4.727295	0.052223
F	-4.838691	-2.920317	-0.240219
O	0.927229	-2.057586	-1.160740
O	1.868363	-0.273228	-2.152096
C	1.815748	-1.498856	-1.776919
C	3.075788	-2.291295	-2.192481
F	2.980734	-3.554545	-1.825450
F	3.235005	-2.235877	-3.511662
F	4.148650	-1.754377	-1.613308
C	0.954619	-1.293138	2.797478
H	0.524662	-2.229033	2.421204
H	1.086455	-1.399839	3.877614
H	1.937868	-1.158247	2.341152
C	0.048213	-0.122957	2.452094
H	0.495837	0.788729	2.881434
O	-0.028219	0.072924	1.068423
H	1.008930	0.231843	-1.899627
C	-1.332027	-0.296539	3.065054
H	-1.972354	0.549640	2.805062
H	-1.284941	-0.368589	4.155061
H	-1.800148	-1.213373	2.689169
C	-2.331430	1.787728	-0.788010
H	-2.676531	2.809624	-0.941679
H	-2.854163	1.085988	-1.432688
H	-2.518537	1.522003	0.255770
C	-0.863849	1.691702	-1.005372
O	-0.355607	0.738540	-1.596966

O	-0.201301	2.701495	-0.520496
C	1.250125	2.632974	-0.441322
H	1.499392	1.588104	-0.251719
C	1.849219	3.136177	-1.733249
H	2.937481	3.068795	-1.682387
H	1.576470	4.180797	-1.898710
H	1.516473	2.550431	-2.591002
C	1.629273	3.458163	0.761737
H	2.711817	3.428366	0.898297
H	1.156151	3.058883	1.659215
H	1.325743	4.499213	0.631964

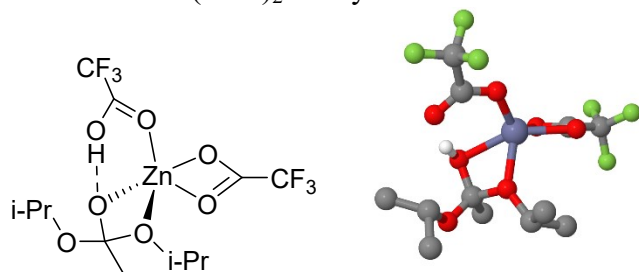
C4. Zn(TFA)₂ catalyzed transition state 2 (nucleophilic attack)



Zn	-0.594362	-1.548969	-0.245752
O	-1.567559	-3.285870	0.357146
O	-2.447828	-1.947723	-1.149774
C	-2.486241	-2.967661	-0.429457
C	-3.752135	-3.843563	-0.469463
F	-4.315931	-3.829712	-1.671333
F	-3.488999	-5.102463	-0.144791
F	-4.636845	-3.360853	0.411762
O	0.959441	-2.083338	-1.355831
O	1.761106	-0.157545	-2.194830
C	1.792019	-1.382538	-1.951725
C	3.074073	-2.096039	-2.447118
F	4.104889	-1.706113	-1.689442
F	2.972130	-3.412240	-2.366177
F	3.337769	-1.768369	-3.708344
C	0.707430	-0.540415	2.844961
H	0.701201	-1.619111	2.656578
H	0.658995	-0.388453	3.926237

H	1.654167	-0.136962	2.479279
C	-0.462308	0.120853	2.136994
H	-0.436738	1.198920	2.368696
O	-0.319778	0.006861	0.747452
H	0.691827	0.456201	-1.859860
C	-1.790896	-0.437303	2.617804
H	-2.623706	0.034372	2.091930
H	-1.926344	-0.272717	3.689669
H	-1.838989	-1.516048	2.436261
C	-2.109233	1.824981	-0.432295
H	-2.461083	2.610331	-1.108346
H	-2.662262	0.911645	-0.637436
H	-2.260568	2.153442	0.592943
C	-0.666092	1.606528	-0.699800
O	-0.346476	0.857049	-1.665232
O	0.116504	2.474826	-0.138253
C	1.562399	2.390178	-0.289389
H	1.817775	1.331214	-0.326319
C	1.982832	3.101536	-1.553470
H	3.066153	3.030385	-1.664295
H	1.708261	4.157466	-1.504244
H	1.529106	2.659519	-2.440395
C	2.135868	3.004064	0.962343
H	3.225460	2.954302	0.926210
H	1.794223	2.467487	1.848008
H	1.840744	4.051842	1.049101

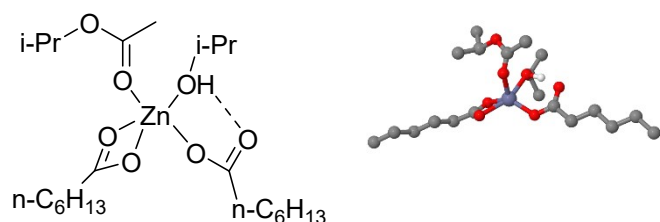
C5. Zn(TFA)₂ catalyzed tetrahedral intermediate



O	-2.514656	0.670731	0.893754
O	-1.461798	-0.987082	-0.195757
C	-2.473449	-0.376768	0.257059
C	-3.809194	-1.080275	-0.089965
F	-3.787866	-2.353375	0.299399
F	-4.842625	-0.484992	0.488167
F	-3.999872	-1.051630	-1.412836

O	2.019207	-1.160265	0.740930
O	1.615218	-1.340342	-1.411897
C	2.324461	-1.552591	-0.412105
C	3.676371	-2.266208	-0.594306
F	3.667321	-3.070289	-1.648023
F	4.622466	-1.336438	-0.786252
F	4.004788	-2.976825	0.476070
Zn	0.330836	-0.305773	-0.035032
O	0.610251	1.650051	-0.641564
C	0.592355	2.297485	0.667120
C	1.980120	2.489817	1.220559
H	2.509779	1.537931	1.244817
H	2.529518	3.210280	0.616644
H	1.892201	2.877057	2.234482
O	-0.011111	3.512347	0.609097
C	-1.404480	3.608166	0.244858
H	-1.708636	2.677163	-0.240846
C	-2.229533	3.836813	1.492094
C	-1.526448	4.751953	-0.735651
O	-0.054602	1.318420	1.423879
C	1.181056	2.326109	-1.785134
C	0.251213	2.074825	-2.949427
H	1.185105	3.389505	-1.530026
C	2.586708	1.839250	-2.059962
H	-1.043504	1.271242	1.255050
H	3.008896	2.403417	-2.894276
H	2.578865	0.782675	-2.332629
H	3.240966	1.973249	-1.198765
H	0.613663	2.594344	-3.838319
H	-0.758962	2.423931	-2.731527
H	0.209968	1.006660	-3.176828
H	-3.288038	3.898231	1.232928
H	-1.930551	4.772511	1.969916
H	-2.110173	3.026548	2.210634
H	-0.943401	4.568237	-1.639202
H	-1.171927	5.678525	-0.278815
H	-2.570612	4.888311	-1.023191

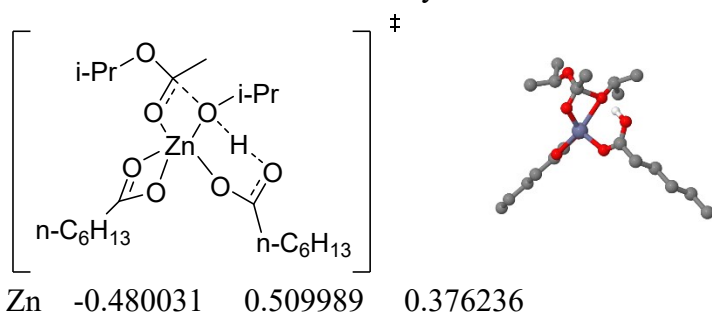
D1. Zinc hexanoate catalyzed attacking complex



Zn	-0.746923	1.070176	0.395141
C	3.301678	0.606760	1.048430
O	0.340191	-0.022139	1.805603
C	2.492655	-0.335515	0.188472
O	1.918237	-1.391727	1.008841
C	3.305893	-1.041770	-0.866211
C	0.852714	-1.128364	1.724010
C	0.305063	-2.310738	2.444879
O	-0.714564	-0.726931	-0.705453
C	-0.773493	-0.768773	-2.132175
C	-2.015927	-0.070241	-2.645343
C	-0.681179	-2.208841	-2.591518
H	4.103485	0.068942	1.559892
H	3.753807	1.372030	0.413998
H	2.673225	1.107167	1.784817
H	-0.678763	-2.523356	2.017280
H	4.123524	-1.608173	-0.414880
H	2.681033	-1.726444	-1.441423
H	1.667169	0.199186	-0.282856
H	0.950166	-3.180688	2.352368
H	3.730787	-0.306067	-1.551194
H	0.154435	-2.049512	3.492685
H	0.107449	-0.215147	-2.468805
H	-2.036042	-0.082053	-3.737356
H	-0.639140	-2.264833	-3.681592
H	-2.033763	0.971008	-2.318382
H	0.213157	-2.685187	-2.184983
H	-2.917146	-0.570641	-2.280821
H	-1.554326	-2.774558	-2.254515
H	-1.563021	-1.091605	-0.285387
H	-6.600457	-0.837438	3.403167
H	-8.775825	-2.005402	4.131494
H	-6.929994	-3.280183	2.992067
H	-4.442936	0.325942	2.682598
H	-4.776082	-2.137176	2.268451
C	-5.364931	-1.387503	1.730725

C	-4.592785	-0.085481	1.678413
C	-6.725927	-1.232447	2.386822
C	-7.515163	-2.529489	2.448431
C	-3.230658	-0.171521	1.032630
C	-8.875150	-2.367735	3.104335
O	-2.812586	-1.265669	0.611080
O	-2.595877	0.932136	0.967624
H	-9.422497	-3.312582	3.136946
H	-5.483955	-1.779609	0.715820
H	-5.152492	0.685032	1.137175
H	-7.639458	-2.922518	1.432788
H	-7.311145	-0.479308	1.843700
H	-9.490691	-1.645617	2.560422
H	3.475570	5.888131	-0.937656
H	5.070865	7.799223	-0.281702
H	4.430917	6.010465	1.368228
H	1.897586	3.957703	-1.584901
H	2.856358	4.126031	0.741865
C	2.123537	4.857832	0.382466
C	1.288452	4.232419	-0.720651
C	2.842817	6.116025	-0.070231
C	3.695187	6.744466	1.019464
C	0.509560	3.021407	-0.291221
C	4.407762	8.005415	0.563315
O	0.099665	2.912089	0.892786
O	0.253286	2.110490	-1.132968
H	5.013414	8.437805	1.362944
H	1.476895	5.077302	1.236109
H	0.551231	4.957933	-1.086583
H	3.061650	6.970157	1.884692
H	2.105793	6.849599	-0.421129
H	3.691908	8.766443	0.240164

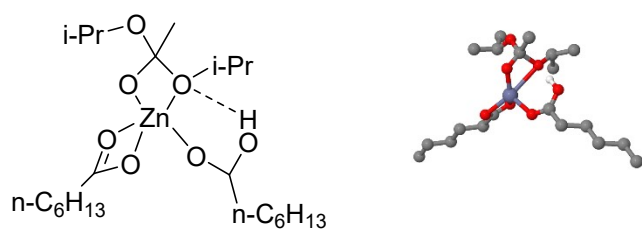
D2. Zinc hexanoate catalyzed transition state



C	3.310096	1.690635	0.855084
O	0.838736	0.112288	1.735190
C	2.888911	0.539866	-0.033417
O	2.741562	-0.662854	0.738361
C	3.911132	0.233760	-1.104083
C	1.563352	-0.887529	1.372500
C	1.742195	-2.018594	2.348103
O	0.539047	-1.550877	0.144541
C	1.087502	-2.360201	-0.893892
C	0.619002	-1.838052	-2.236147
C	0.726652	-3.821123	-0.692995
H	3.432590	2.597117	0.257411
H	2.562735	1.876796	1.624527
H	4.265907	1.463814	1.334387
H	2.320686	-1.639023	3.192588
H	3.573751	-0.576450	-1.752408
H	4.080093	1.118160	-1.721434
H	1.933447	0.771343	-0.514623
H	0.772924	-2.356331	2.709757
H	4.861635	-0.057104	-0.650645
H	2.286928	-2.846874	1.896834
H	2.175163	-2.251390	-0.825774
H	-0.467467	-1.928506	-2.323070
H	-0.351505	-3.975438	-0.785759
H	1.072862	-2.412171	-3.047678
H	1.221399	-4.436957	-1.447381
H	0.873953	-0.785472	-2.362040
H	1.038652	-4.174920	0.291375
H	-0.623545	-2.090373	0.751123
H	-5.963038	-3.662651	1.474882
H	-8.216822	-4.572428	0.624750
H	-6.313243	-4.122797	-0.956870
H	-3.717025	-2.774371	2.305248
H	-4.086231	-3.232821	-0.121341
C	-4.612104	-2.408186	0.371535
C	-3.806082	-1.954506	1.590141
C	-6.017333	-2.847356	0.743098
C	-6.834782	-3.299518	-0.455518
C	-2.438878	-1.520874	1.171447
C	-8.239687	-3.736873	-0.080318
O	-1.536242	-2.439789	1.169328
O	-2.241675	-0.351955	0.811510
H	-8.807417	-4.057071	-0.956534

H	-4.659877	-1.586643	-0.350547
H	-4.302098	-1.109356	2.070187
H	-6.884480	-2.483477	-1.185264
H	-6.535164	-2.021485	1.245834
H	-8.792250	-2.921175	0.394050
H	-0.210299	6.154371	-2.856435
H	-0.643151	8.666734	-3.209567
H	-0.770421	7.630832	-0.920076
H	0.222616	3.658375	-2.509836
H	-0.344219	5.150821	-0.557864
C	-1.086836	4.920106	-1.327956
C	-0.735709	3.599259	-1.982937
C	-1.167303	6.061237	-2.326924
C	-1.516386	7.394701	-1.687509
C	-0.650931	2.428548	-1.046764
C	-1.596466	8.531878	-2.690668
O	-0.920098	2.546754	0.174272
O	-0.299024	1.298059	-1.508154
H	-1.848194	9.478653	-2.207475
H	-2.038867	4.818542	-0.798626
H	-1.468576	3.334009	-2.753222
H	-2.471934	7.299913	-1.159226
H	-1.913269	5.823289	-3.096195
H	-2.357987	8.333591	-3.450275

D3. Zinc hexanoate catalyzed tetrahedral intermediate



Zn	-0.741880	0.849220	0.419526
C	2.868909	1.852877	0.981562
O	0.423504	0.118767	1.715795
C	2.581199	0.687954	0.056132
O	2.440076	-0.524230	0.799187
C	3.702515	0.460905	-0.934551
C	1.176783	-0.866476	1.261130
C	1.375311	-1.994793	2.249754
O	0.380784	-1.398109	0.069163

C	1.014824	-2.238881	-0.905102
C	0.692530	-1.685484	-2.276635
C	0.564929	-3.678813	-0.747918
H	2.965417	2.777574	0.406604
H	2.068337	1.972060	1.709776
H	3.806444	1.680942	1.516789
H	1.866785	-1.587187	3.132938
H	3.467356	-0.357030	-1.617928
H	3.873181	1.363368	-1.525320
H	1.658880	0.879940	-0.504012
H	0.408746	-2.405742	2.540260
H	4.627031	0.214304	-0.406849
H	2.004478	-2.781008	1.831468
H	2.090182	-2.168423	-0.724298
H	-0.382941	-1.737144	-2.466615
H	-0.505573	-3.778570	-0.945082
H	1.203026	-2.263739	-3.050250
H	1.098129	-4.314602	-1.458223
H	0.993151	-0.640622	-2.359398
H	0.765102	-4.051445	0.257745
H	-0.985743	-1.857862	0.533567
H	-6.104057	-3.497894	1.905211
H	-8.027226	-5.173136	1.559225
H	-5.874147	-5.379156	0.275138
H	-4.194193	-1.857469	2.249240
H	-3.965858	-3.732617	0.627833
C	-4.658981	-2.911012	0.428537
C	-4.190339	-1.665602	1.169308
C	-6.068667	-3.314278	0.824029
C	-6.563686	-4.548127	0.088026
C	-2.800348	-1.236769	0.821815
C	-7.971627	-4.950482	0.490041
O	-1.921868	-2.187360	0.804666
O	-2.546207	-0.054410	0.579440
H	-8.305303	-5.838023	-0.051775
H	-4.620213	-2.726854	-0.650943
H	-4.852647	-0.817775	0.990417
H	-6.527122	-4.361548	-0.991354
H	-6.755750	-2.480017	0.636337
H	-8.684521	-4.147331	0.283762
H	-0.082247	6.240378	-3.157869
H	0.064527	8.787737	-3.494250
H	0.530710	7.738708	-1.255348

H	-0.207146	3.696081	-2.818174
H	0.381847	5.231795	-0.904385
C	-0.625320	5.232515	-1.335811
C	-0.892373	3.888641	-1.989354
C	-0.762079	6.389935	-2.309326
C	-0.481445	7.742318	-1.675907
C	-0.826082	2.719398	-1.051425
C	-0.625333	8.896324	-2.652489
O	-1.086756	2.862502	0.174666
O	-0.523872	1.573158	-1.497784
H	-0.417877	9.856523	-2.174802
H	-1.311518	5.363004	-0.494777
H	-1.900735	3.875802	-2.422058
H	-1.159709	7.888945	-0.827674
H	-1.774856	6.392007	-2.732506
H	-1.638434	8.940847	-3.062194

Stress relaxation time fitting

Figure S3 shows the stress relaxation tests. The stress relaxation fittings were conducted according to our previous work and others,^{2,3} and the fitting parameters are presented in Table S2-S5.³ The Kohlrausch-Williams-Watts (KWW) stretched exponential decay is given below (1):

$$\frac{\sigma(t)}{\sigma_0} = \left[A_{net} \exp\left\{ - \left(t / \tau_{net} \right)^{\beta_{net}} \right\} + A_{ex} \exp\left\{ - \left(t / \tau_{ex} \right)^{\beta_{ex}} \right\} \right] \quad (1)$$

where $\sigma(t)/\sigma_0$ is the normalized stress at time t , τ is the characteristic relaxation time, A is the contribution of two relaxation components such that $A_{net} + A_{ex} = 1$, and β is the exponent which controls the shape of the stretched exponential decay.^{2,4,5}

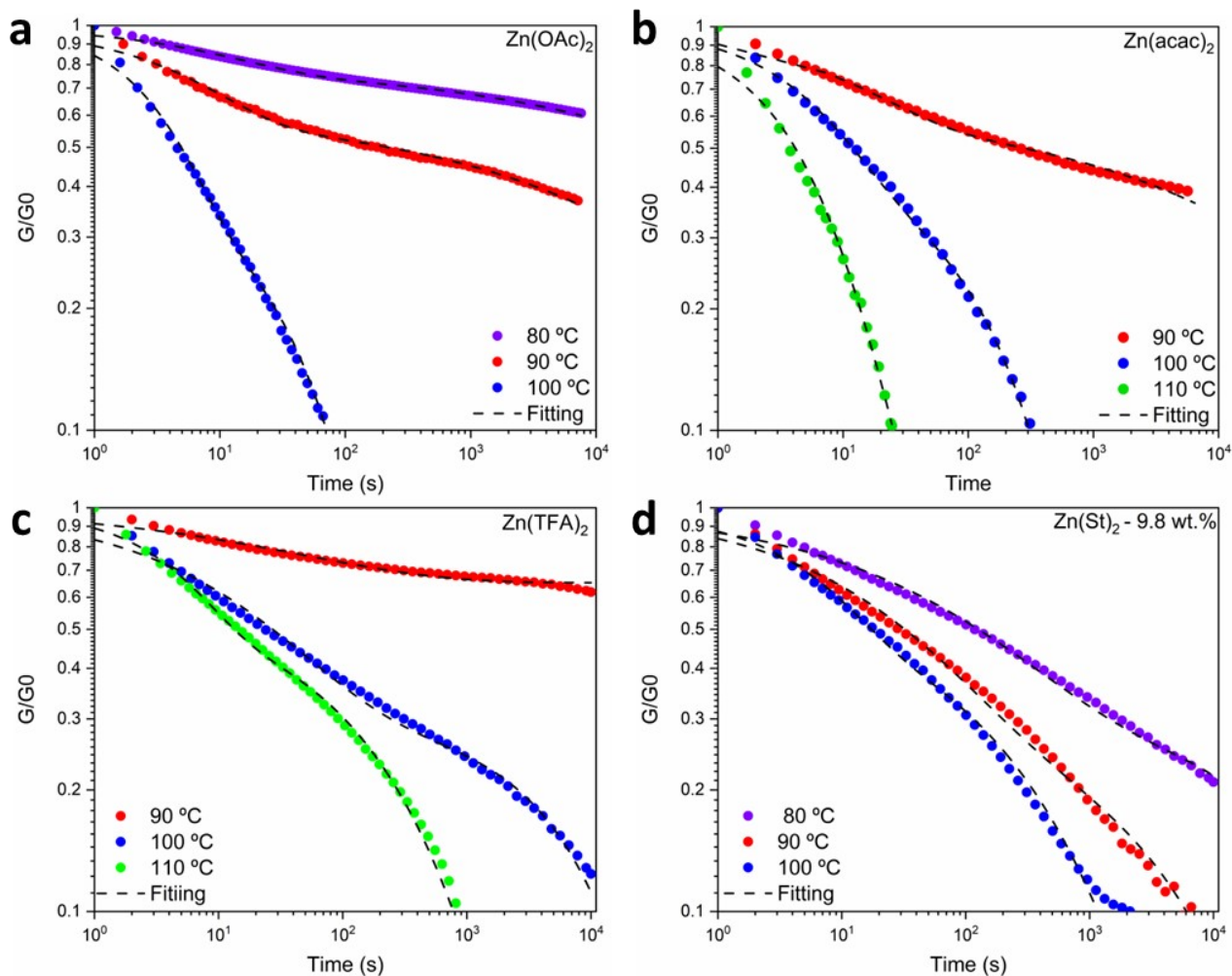


Figure S3 Stress relaxation curves of vitrimerized EVA with a) $\text{Zn}(\text{OAc})_2$, b) $\text{Zn}(\text{acac})_2$, c) $\text{Zn}(\text{TFA})_2$, and d) $\text{Zn}(\text{St})_2 - 9.8 \text{ wt.}\%$.

Table S3. Parameters obtained from fitting stress relaxation curves to experimental data for vitrimerized EVA with zinc trifluoroacetate using equation 1.

T (°C)	τ_{net} (seconds)	τ_{ex} (seconds)	β_{net}	β_{ex}	A_{net}	A_{ex}	R ²
90	4.64E28±0.00	33.67±0.11	1.00±0.00	0.35±0.00	0.65±0.00	0.35±0.00	0.97
100	1.03E4±6.06E1	17.70±0.11	0.67±0.01	0.46±0.00	0.30±0.00	0.70±0.00	0.99
110	2.38E2±1.69	5.79±0.10	0.48±0.00	0.96±0.00	0.59±0.00	0.41±0.00	1.00

Table S4. Parameters obtained from fitting stress relaxation curves to experimental data for vitrimerized EVA with zinc acetylacetonate using equation 1.

temperature (°C)	τ_{net} (seconds)	τ_{ex} (seconds)	β_{net}	β_{ex}	A_{net}	A_{ex}	R ²
90	6.01E4±4.95E2	14.35±0.07	0.26±0.00	0.64±0.00	0.64±0.00	0.36±0.00	0.99

100	1.64E2±1.66E0	6.97±0.02	0.66±0.00	0.80±0.00	0.46±0.00	0.54±0.00	1.00
110	2.88E1±1.25E2	4.87±2.37	0.93±3.08	0.81±0.02	0.20±0.90	0.80±0.90	0.97

Table S5. Parameters obtained from fitting stress relaxation curves to experimental data for vitrimerized EVA with zinc acetate using equation 1.

T (°C)	τ_{net} (seconds)	τ_{ex} (seconds)	β_{net}	β_{ex}	A_{net}	A_{ex}	R^2
80	8.06E5±2.09E4	12.44±0.03	0.27±0.00	0.65±0.00	0.80±0.00	0.20±0.00	0.99
90	7.53E4±6.05E2	7.62±0.02	0.26±0.00	0.73±0.00	0.62±0.00	0.38±0.00	0.99
100	4.60E1±0.76	3.94±0.01	0.74±0.01	1.00±0.00	0.40±0.00	0.60±0.00	0.99

Table S6. Parameters obtained from fitting stress relaxation curves to experimental data for vitrimerized EVA with zinc stearate using equation 1.

T (°C)	τ_{net} (seconds)	τ_{ex} (seconds)	β_{net}	β_{ex}	A_{net}	A_{ex}	R^2
80	5.94E4±8.41E3	96.19±1.95	1.00±0.11	0.36±0.00	0.25±0.01	0.75±0.00	0.99
90	5.07E3±2.44E2	24.71±0.38	0.48±0.01	0.43±0.00	0.30±0.01	0.70±0.01	0.99
100	2.43E2±0.00	8.21±0.03	0.39±0.00	0.84±0.01	0.63±0.00	0.37±0.00	0.99

Figure S4 shows the Arrhenius plot of measured average relaxation times using equation (2) and (3):^{2,3}

$$\langle \tau \rangle = \frac{\tau_{ex} \Gamma\left(\frac{1}{\beta_{ex}}\right)}{\beta_{ex}} \quad (2)$$

$$\tau^*(T) = \tau_0^*(T) \exp\left(-\frac{E_{ex}}{RT}\right) \quad (3)$$

where $\langle \tau \rangle$ is the average characteristic relaxation time and $\tau^*(T)$ corresponds to $\langle \tau \rangle$ at the test temperature, E_{ex} is the flow activation energy of exchange reaction, R is the universal gas constant, and T is the absolute temperature.

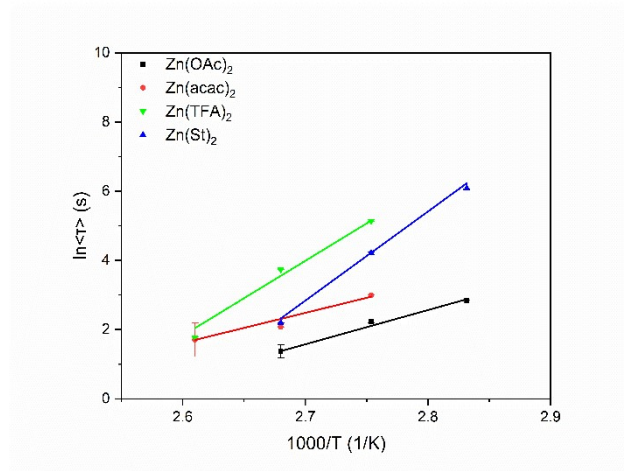


Figure S4 Arrhenius plot of the measured average relaxation times for $\text{Zn}(\text{OAc})_2$, $\text{Zn}(\text{acac})_2$, $\text{Zn}(\text{TFA})_2$ and $\text{Zn}(\text{St})_2 - 9.8 \text{ wt.}\%$.

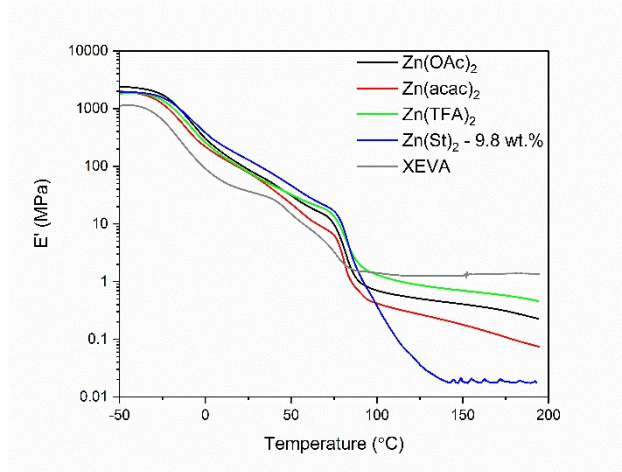


Figure S5. DMA of vitrimerized samples with $\text{Zn}(\text{OAc})_2$, $\text{Zn}(\text{acac})_2$, $\text{Zn}(\text{TFA})_2$ and $\text{Zn}(\text{St})_2 - 9.8 \text{ wt.}\%$ compared with initial crosslinked EVA.

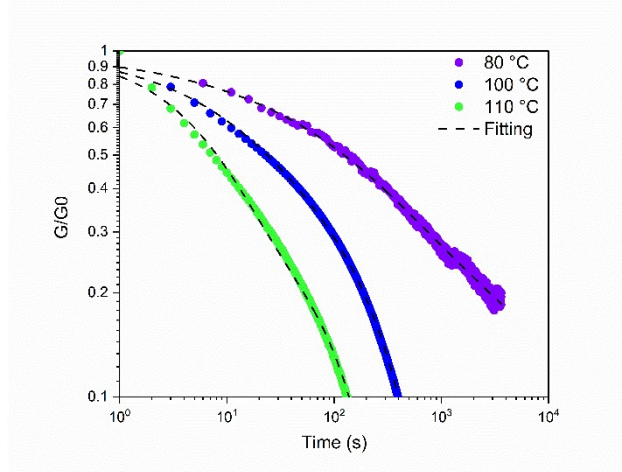


Figure S6 Stress relaxation of $\text{Zn}(\text{St})_2 - 3.1 \text{ wt.}\%$ at different temperatures.

Table S7. Parameters obtained from fitting stress relaxation curves to experimental data for vitrimerized EVA with $\text{Zn}(\text{St})_2 - 3.1 \text{ wt.}\%$ using equation 1.

T (°C)	τ_{net} (seconds)	τ_{ex} (seconds)	β_{net}	β_{ex}	A_{net}	A_{ex}	R^2
80	$1.15\text{E}4 \pm 2.05\text{E}4$	98.08 ± 7.49	0.35 ± 0.11	0.42 ± 0.03	0.35 ± 0.22	0.65 ± 0.22	0.99
100	$2.63\text{E}2 \pm 1.99\text{E}1$	12.25 ± 1.15	0.85 ± 0.04	0.56 ± 0.01	0.41 ± 0.03	0.59 ± 0.03	0.99
110	$1.31\text{E}2 \pm 9.50\text{E}0$	6.91 ± 0.31	0.99 ± 0.06	0.74 ± 0.02	0.28 ± 0.02	0.72 ± 0.02	0.99

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