Harnessing Entropy to Direct the Bonding/Debonding of Polymer Systems Based on Reversible Chemistry

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1. Materials

Isophorone bis(sorbic carbamate) (IPDI-SA) (Evonik Industries AG), *n*-butyl acrylate (*n*BA) (Arkema), bis(bromoisobutyryloxy) butane (Evonik Industries AG), copper(I) oxide, N,N,N',N",N''-pentamethyldiethylenetriamine (PMDETA) (Huntsman), zinc dust (Fluka), sodium iodine, triphenylphosphine, acetic acid, acetone, tetrahydrofuran (THF) methanol, ethanol, chloroform, dimethyl sulfoxide (DMSO) (≥ 99%), 1,2,4-Trichlorobenzene (TCB) (99%), and butylated hydroxytoluene (≥ 99.8%, Roth) were used as received. Toluene was stored over molecular sieves. Isobornyl acrylate (iBoA) (Evonik Industries AG) was distilled and stored at -18°C and 2-2'-azoisobutyronitrile (AIBN) (Fluka) was recrystallized and stored at -18°C. Zinc chloride was vacuum dried and stored under nitrogen. The synthesis of 1,4-phenylenebis(methylene)bis((diethoxyphosphoryl)methanedithio-formate) (P-di-linker) was synthesized as described in the literature.[1]

2. *Ab inito* molecular orbital theory

Theoretical calculations were performed using Gaussian09[2] and MOLPRO 10.[3] Optimized geometries and harmonic frequencies were obtained at the M06-2X/6-31G* level of theory.[4] The lowest energy conformer for the IPDI-SA diene and the P-di-linker (n=m=0) was located using the energy directed tree search (EDTS) algorithm[5], also at the M06-2X/6-31G* level. The corresponding solution-phase structure was obtained by re-optimizing the gas phase conformers that are within 5 kJ mol^{-1} of the global minimum using the SMD continuum model[6] and toluene as the solvent. There are a number of possible diastereomers for IPDI-SA and the Diels-Alder product, but all calculations are based on the lowest energy diastereomer. For the Diels-Alder product, the lowest energy diastereomer was determined using a smaller model compound, and is depicted in Supplementary Figure S1. The gas phase reaction energies (ΔE_{rxn}) were obtained at the G3(MP2) level[7] using an ONIOM approximation[8, 9], in which the isodesmic full reaction was calculated at the M06-2X/6-31G* level. The reaction core employed in the ONIOM calculation is shown in Supplementary Figure S2. The temperature-dependent solvation free energies of each species in toluene was calculated using the COSMO-RS model[10, 11] at the BP/TZP level of theory as implemented in the ADF program.[12, 13]

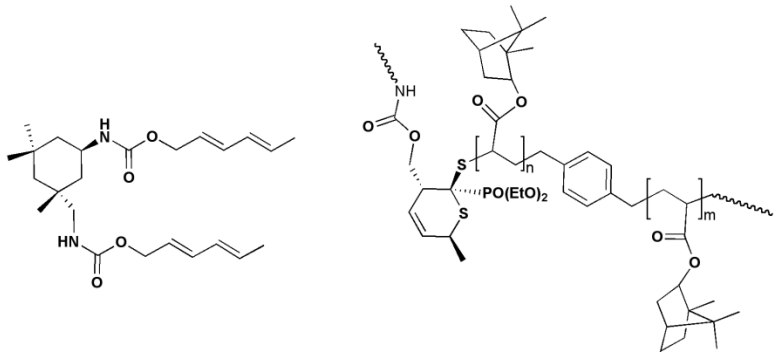

Figure S1. The stereochemical structures of the reactant diene (*i.e.*, IPDI-SA) and the DA product of IPDI-SA + P-di-linker.

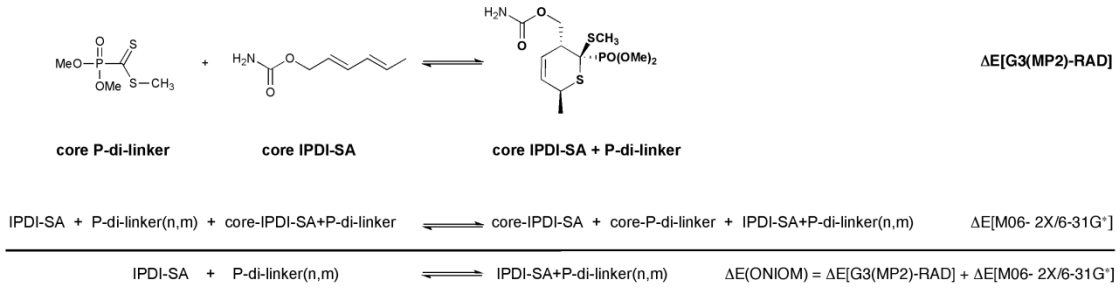

Figure S2. The ONIOM scheme for calculating G3(MP2)-RAD reaction energies.

Gaussian archives

IPDI-SA

```
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,0.7619196796,-0.4254506212\H,-9.4032745528,-2.4563998947,-2.460730345
2\H,-9.5417106923,-0.8943493352,-1.6504510377\H,-8.9018116764,-2.29192
00867,-0.7792833281\H,-6.7920242567,-0.4024842395,-4.095359356\H,-8.40
89505369,0.0826138135,-3.5754294866\H,-8.1612537124,-1.4930392625,-4.3
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55234774,-1.8270106191\H,-0.2757302697,-1.2768005874,-2.6880059624\C,0
.9248075384,-2.6565812143,-1.5111455393\H,1.499800557,-2.6539460402,-0
.5810891238\H,1.6021723356,-2.9201025362,-2.328166628\H,0.1438123808,-
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,-1.5101844406,2.8999596065,-1.5523563245\H,-2.6711657406,2.3875599615
,-2.7969614373\C,-0.5854949343,2.2395973475,-3.4039133916\H,-0.5671913
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08,-3.0906570152\H,7.4085557547,-3.893324499,-2.8493859844\H,5.7459337
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0988\H,6.8804786966,-2.1229611425,-4.5423131493\H,5.2239953568,-2.7444
716612,-4.6793768802\H,6.5921306506,-3.738280054,-5.2247002973\C,7.887
6932892,-3.9477222537,0.848550401\H,7.0948853855,-4.070786599,1.590596
7193\H,8.7222800032,-3.4187398996,1.312670335\C,8.3080386923,-5.280882
1952,0.2648469211\H,9.0715904371,-5.1361059514,-0.5047098074\H,7.44188
295,-5.7815610094,-0.1763154842\H,8.7214182875,-5.9232686954,1.0479604
351\\Version=EM64L-G09RevA.02\State=1-A\HF=-4744.2579603\RMSD=4.128e-0
9\RMSF=1.371e-06\ZeroPoint=1.0958812\Thermal=1.1616578\Dipole=0.14636,
0.3171078,-1.2879462\PG=C01 [X(C44H68O10P2S4)]\@

P-di-linker (n=m=2)

1\1\GINC-V1282\Freq\RM062X\6-31G(d)\C70H108O14P2S4\JMH502\21-Nov-2012\
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maxdisk=157286400\\dienophile-n2m2-trimmed.freq\\0,1\C,-3.8827337294,-
5.6632548977,-1.268775219\C,-2.5971917374,-5.0525443749,-0.7614324331\
C,-1.3902394194,-5.2404053048,-1.4403653419\C,-0.2136489901,-4.6481703
117,-0.9920537722\C,-0.2069026646,-3.8265253085,0.1393788138\C,-1.4179
228944,-3.6167280335,0.8036661604\C,-2.5892624713,-4.2350255939,0.3734
246366\C,1.0660336008,-3.2089292341,0.670758798\H,-1.3706471766,-5.874
6735138,-2.3244127545\H,-3.5178518149,-4.0822118069,0.9223265118\H,-1.
4381266388,-2.9613661901,1.6715497092\H,0.7154939039,-4.8396808269,-1.
5242973464\H,0.8145988992,-2.57023701,1.5182861113\H,1.7321411844,-3.9
992778604,1.0449742357\H,-4.5449308702,-5.8909902958,-0.4307629494\H,-
3.6627019104,-6.6050910097,-1.7840336548\C,-4.6218574496,-4.7402071144
,-2.2602715861\H,-3.9758385331,-4.5871958846,-3.1334033396\H,-5.531943
1834,-5.2375959211,-2.616077351\C,-4.9593830732,-3.3516452674,-1.69336
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77773041,-2.7475691747\H,-4.5213197816,-2.4338624782,-3.6105084213\H,-
6.1994724227,-2.2393503167,-3.1178903032\P,-0.9756037745,0.2691069773,
-0.1257910861\O,-0.2525318272,-0.428548581,0.9585486674\O,-0.369875906
8,0.2303271788,-1.5920515113\O,-1.2101547544,1.831294581,0.1191746439\
C,-2.6782365828,-0.3543342022,-0.427521199\S,-3.6330908144,-0.53159804
65,0.8834750783\S,-3.048642883,-0.5986978483,-2.1048824629\C,-4.850416
448,-0.9127760824,-2.1023458894\C,-5.5058522756,0.3013093996,-2.726866
6034\O,-5.4010489542,1.3305521426,-1.8778170653\C,-5.7138594473,2.6346
924921,-2.3844798885\C,-4.7152472687,3.1116642678,-3.4699378388\C,-4.1
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6443266\C,-4.1597843706,3.4138332631,-0.6094695567\C,-5.5528457838,3.6
549092999,-1.2383168405\C,-5.3112358219,4.9666665129,-2.0523166132\C,-
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,0.348414225,-3.816749392\H,-5.1362686151,-0.9253269814,-1.0476484726\
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,-3.5504331824\H,-2.5103826274,3.0870997513,-2.0416480391\H,-3.9587748
642,2.3452572701,-3.667547974\H,-6.7424379461,2.6001689495,-2.75637990
05\H,-4.0140211521,2.3661960058,-0.335980291\H,-2.5230772227,4.7010070
281,-1.339863109\H,-5.2271849761,3.3152105399,-4.413191611\H,-6.560233
7808,4.3875774559,0.5357186298\H,-6.7485274995,2.649918331,0.246989239
8\H,-7.661060079,3.8094405261,-0.7333779218\H,-6.1947366402,6.22904189
56,-3.5756463738\H,-7.3319544869,5.7153813267,-2.3267423246\H,-6.85061
81859,4.5923777223,-3.6013162331\H,-4.1153176067,5.9986683455,-0.50967
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9761466631,-2.412645949,-0.8180070794\C,-8.1220074176,-2.3870370696,0.
050708379\C,-9.3252163367,-1.7631141767,-0.6959134091\C,-9.7668725596,
-0.6249098892,0.2466010953\C,-8.7364839888,0.5089330262,0.0919284746\C
,-7.4722038369,-0.0906180715,0.7678099316\C,-7.9313715442,-1.475732086
3,1.2824656688\C,-9.4269685121,-1.1995823006,1.6493438515\C,-7.0384754
355,-2.0665260649,2.3573636362\C,-10.2382979537,-2.4464779083,2.021684
7387\C,-9.6019576026,-0.1962105598,2.7930594189\O,-6.2028174804,-4.288
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02994333\H,-9.0125277668,-1.3866083982,-1.674663022\H,-8.3057315763,-3

.4160983629,0.3648200633\H,-6.6300184237,-0.1731159979,0.0787533716\H,
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,-0.8624483564\H,-6.9988476304,-1.4088819449,3.233125559\H,-6.01568329
74,-2.188489074,1.9840558635\H,-7.3889078288,-3.0546082966,2.673591725
4\H,-11.2773996209,-2.1645131037,2.2249693438\H,-9.8392410488,-2.90408
06091,2.9337898157\H,-10.2557531697,-3.2149960815,1.2459881607\H,-9.00
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5700167\H,-10.6525132258,0.107874284,2.8643637259\C,1.8261835704,-2.37
79192435,-0.3644516852\H,1.1490415996,-1.6489605112,-0.8235009344\H,2.
1829504271,-3.0287592213,-1.1732883208\C,3.0623049356,-1.6418129277,0.
1976550801\H,3.6406774017,-2.3427649264,0.8126133457\C,3.9326203669,-1
.1645986366,-0.9698210865\H,3.3176628241,-0.6703092075,-1.7304004233\H
,4.3556416837,-2.0595578504,-1.4362117883\C,5.0571582754,-0.1960271696
,-0.5846011202\S,6.5921332124,-0.5022066717,-1.5431186046\C,7.22669558
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,5.0982486915,6.3144361667,-1.0824662689\O,8.4080417614,-3.8395556785,
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,-0.667343404\H,10.8242959117,-4.9666371917,-1.7220043284\H,11.3786241
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2,2.8315886197\H,7.0114410429,3.4302905468,0.9600452495\H,5.3772423653
,3.5615786849,-1.4828909318\H,3.860286209,2.7610065557,1.6967127463\H,
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31287453\C,1.7691391971,0.0395115866,3.2309117968\C,2.823583059,1.0030
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0372036993,3.5426083603\H,-0.3256779006,-0.1879366355,6.9332267686\H,0
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167243,-1.932105886\H,1.5738590154,0.8589764538,-1.1701989536\H,0.5097
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9585,-4.0526827447\H,1.48882843,-0.5034374481,-3.287212128\C,-1.108520
4652,2.3948289076,1.4434103252\H,-1.1737328971,1.5950134509,2.18886723
44\H,-1.976903701,3.0494310265,1.5514208809\C,0.1973476246,3.154895236
1,1.5485520235\H,0.2691824782,3.6599610442,2.5176002643\H,0.2513548802
,3.9117844699,0.7611957421\H,1.0497340401,2.473212789,1.434549117\C,10
.4027722412,-1.5370637658,-3.224939304\H,11.2397733297,-1.878937833,-2
.6061046987\H,10.1665156442,-2.3111847443,-3.9611873424\C,10.700683946
2,-0.2070805169,-3.8800112072\H,11.5686822529,-0.3008602806,-4.5380908
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22,-4.473583471\\Version=EM64L-G09RevA.02\State=1-A\HF=-6059.5134127\R
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ole=0.7255136,2.2098556,0.475036\PG=C01 [X(C70H108O14P2S4)]\@

Diel-Alder Product (n=m=0)

1\1\GINC-X152\Freq\RM062X\6-31G(d)\C42H66N2O10P2S4\JMH502\15-Oct-2012\
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590396,-0.2504242253,1.1683934183\C,3.6423768858,0.1176340673,-1.20785
43618\H,5.2526677184,-0.7610202633,-2.3283786319\H,5.3323318517,-1.423
1685196,1.9088360336\H,3.244702923,-0.1100292828,2.1508926825\H,3.1590
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905193\S,0.4148869418,-0.0695264556,-0.0778559725\C,-1.0786923068,0.98
72317383,-0.2369168699\C,9.4613866076,-1.8630422872,-0.4681830936\S,9.
4394932164,-3.4838804409,-0.6736483843\P,-1.2249085074,2.2537420895,1.
093434274\O,-2.5508318278,2.9118900958,1.1818908958\O,-0.7434843923,1.
4633255381,2.3995427931\O,-0.0138719272,3.289185199,0.8890837568\C,-0.
8924971568,2.1322004977,3.6691130561\H,-1.9440466566,2.4055360645,3.79
92136183\H,-0.290089785,3.0478394069,3.6509396359\C,-0.4205506061,1.17
65817527,4.7424397536\H,0.6251467638,0.9045530133,4.578278587\H,-1.023
6715351,0.2654181842,4.7300093441\H,-0.5118407307,1.6432291666,5.72685
32017\C,-0.2549940581,4.5978059001,0.3375702588\H,-1.0746693693,4.5523
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156693045,-2.725545772,-0.0628964869\H,13.0978816405,-3.4987819189,0.7
034716535\H,12.6468630896,-3.1824796459,-0.9845808554\C,14.3293288533,
-2.0064693636,-0.2913893024\H,15.0993034399,-2.716877785,-0.6065651276
\H,14.662092288,-1.5191630159,0.6295137366\H,14.2080291681,-1.25328175
3,-1.0745972847\C,1.7969141,1.1012644278,0.2004608372\H,1.7137424018,1
.5317160091,1.2001735683\H,1.7343450325,1.9068188793,-0.5356519268\C,6
.7071322616,-1.9636059226,-0.3728008973\H,6.777701479,-2.4679354099,-1

.3408844669\H,6.8219650232,-2.7203064731,0.4082141699\S,-0.9526648265,
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\H,-1.9121995486,-0.8907876424,-0.8140039756\C,-2.633444182,2.61043144
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25644\C,-3.5213307883,0.4766516164,-0.9420776473\H,-4.3901120483,-0.16
10477762,-0.8078810383\C,-2.7838766644,3.2061230188,-3.352408729\H,-2.
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222548928\H,-2.7245706013,2.4288711506,-4.1198933261\C,-2.6099527403,-
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1.6992127307,-0.7573589549,1.7182048564\O,-3.3074820389,-1.7781857185,
1.0542847433\C,-4.6600218689,-1.7458719178,1.1465327643\O,-5.316464061
,-0.7341215539,1.2746509977\N,-5.1672381044,-3.0085424302,1.0789875089
\H,-4.4999732329,-3.7205651041,0.8049525585\C,-6.5470969107,-3.1885977
07,0.6337920141\C,-8.012081126,-3.3618438289,-1.4776142129\C,-8.566572
6592,-4.736056048,0.7182591599\C,-8.6756395417,-4.5899632466,-0.820839
4083\C,-7.1110524461,-4.5036843757,1.1627560512\C,-6.605262724,-3.1735
985021,-0.8954979265\C,-9.4991176509,-3.7909476121,1.4976698823\H,-8.2
064240805,-5.4815319631,-1.2626248123\H,-6.484593905,-5.3287642844,0.7
868286691\H,-5.9716566783,-3.9971701574,-1.2601325354\H,-7.1025438674,
-2.3371408432,1.0404377608\C,-7.8810227963,-3.6127786873,-2.9861211245
\C,-8.9709092964,-6.1734791373,1.070782633\H,-9.7362878575,-4.63158205
16,-1.1111698295\H,-7.0467176146,-4.5239788419,2.2574843337\H,-6.16245
49405,-2.2423429165,-1.2694675306\C,-8.9041866193,-2.1090215427,-1.283
6234345\H,-9.326452333,-2.0660569565,-0.2824704098\H,-9.7471765871,-2.
1781637626,-1.9836731833\N,-8.2258149779,-0.8451990776,-1.4639061957\H
,-7.7930529071,-0.6048307945,-2.3440894764\C,-7.9331831104,-0.05512457
49,-0.3901223132\O,-8.3415792944,-0.243784551,0.7379341984\O,-7.156061
6088,0.9784653243,-0.7712121341\C,-6.7924023995,1.8993289975,0.2773109
718\H,-5.9190085864,1.4980904181,0.7996777053\H,-7.6268630322,1.951882
9746,0.9831459651\C,-6.501345085,3.2247879823,-0.346840413\H,-7.276471
9875,3.6530819566,-0.9826043985\C,-5.3564695512,3.8770038819,-0.117655
0649\H,-4.5974301872,3.4095942569,0.5106250256\C,-5.0073487182,5.18140
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9001686\C,-3.3996909205,7.1078061742,-0.921792735\H,-2.4544441386,7.01
31459537,-1.471318737\H,-3.2242728621,7.826306872,-0.1122309374\H,-4.1
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78834727\H,-10.0133139971,-6.3638421518,0.790321678\H,-8.3407423751,-6
.9026933355,0.5495856984\H,-9.5627806627,-4.1224547297,2.5402852375\H,
-9.1600303987,-2.7515973515,1.5159410258\H,-10.5130025463,-3.813203275
4,1.0813102712\H,-7.4438098879,-2.7444542464,-3.4949812719\H,-7.235014
8009,-4.4730550106,-3.1900945723\H,-8.8608585162,-3.8091914671,-3.4360
104261\\Version=EM64L-G09RevA.02\State=1-A\HF=-4776.2978313\RMSD=5.874
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9647,0.6786039,0.5000956\PG=C01 [X(C42H66N2O10P2S4)]\@

Diels-Alder Product (n=m=1)

1\1\GINC-V1411\Freq\RM062X\6-31G(d)\C68H106N2O14P2S4\JMH502\12-Oct-201
2\0\\#M062X/6-31G* INT(grid=ultrafine) IOP(2/17=4) Freq=noraman
maxdisk=6039797760\\ch3.freq\\0,1\P,-3.8100354478,0.7168516865,-0.5365
704698\O,-2.9437595238,1.4855201714,0.3853815808\O,-3.1089546452,-0.20
84952955,-1.6239196584\O,-4.8053978842,1.6075911973,-1.4108435404\C,-4
.9042282989,-0.4908890327,0.3091095881\S,-5.9162425322,0.1141178584,1.

4401244893\S,-4.6699709245,-2.119954017,-0.2032567142\C,-5.7842945604,
-3.0992801878,0.8671832557\C,-5.1143425433,-4.4206376979,1.2638048343\
C,-4.2314052004,-4.3145199237,2.5203478669\C,-3.1883829127,-3.22936734
05,2.4130165061\C,-2.0535802626,-3.3962955184,1.6121137145\C,-1.185251
3915,-2.3357765288,1.3738264811\C,-1.4165527758,-1.0725854575,1.934752
7498\C,-2.5323910854,-0.9204355387,2.7591725519\C,-3.396987331,-1.9837
625568,3.0055393197\C,-0.5151740775,0.1087238742,1.6583812858\C,-0.069
056293,0.1704832776,0.1961738165\C,0.6223718292,1.4912604459,-0.168394
4491\S,1.4522009697,1.4360286461,-1.8048667898\C,3.0034711027,0.450528
1439,-1.5979807803\S,2.5655272636,-1.3455352187,-1.6549936928\C,4.2275
586847,-2.1048885083,-1.7943871505\C,5.0240752313,-1.4323297785,-2.870
3033317\C,4.8509242124,-0.1913107238,-3.3155059889\C,3.8269952604,0.82
73146668,-2.8704293041\C,4.4585702319,2.2325633303,-2.8314387814\O,5.4
461585226,2.3441647755,-1.8195886931\C,6.718396061,1.9426061516,-2.110
7480812\N,7.3958365973,1.777043917,-0.9365991999\C,8.4084681274,0.7173
161869,-0.8266115599\C,9.7954107352,1.1013605128,-1.3281595689\C,10.83
29230889,0.0149064553,-0.9633439267\C,10.3233013066,-1.3979242185,-1.3
59968067\C,8.8452285445,-1.7628032617,-1.0904931596\C,7.9672628897,-0.
5807230569,-1.5019249935\C,8.5870410185,-2.1262827242,0.3894989103\N,7
.1775356199,-2.3128074304,0.6954589288\C,6.645013216,-3.5469911248,0.8
560044003\O,5.3108954257,-3.4554518266,1.1139321346\C,4.6781363669,-4.
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8008768921,-4.3020885421,3.034264905\C,1.4502791234,-3.8850036631,3.39
25274363\C,1.0767303173,-3.5766752108,4.6401647528\C,-0.2842969792,-3.
0833396036,5.020796708\P,3.835781406,0.735984212,0.0330624624\O,2.8250
47509,0.1513170381,1.1320625502\C,-0.3694367838,2.6371458776,-0.270760
6718\O,-0.5826934694,3.1900143348,0.9232977561\C,-1.6099383359,4.19757
24671,0.9682562028\C,-1.1513343456,5.5608498795,0.3958848613\C,-1.3822
953031,6.5170238194,1.5829889597\C,-0.2667794178,6.2320885352,2.608481
5733\C,-0.6647692905,4.8394404738,3.1734445925\C,-1.9774456329,4.49519
47671,2.4322908639\C,-2.6341634478,5.9043733185,2.2693247759\C,-7.1052
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386175\C,-8.8215011303,-2.2343480462,-1.0615549266\C,-8.6109535757,-2.
8496435904,-2.4677411781\C,-9.0925870188,-1.7237023359,-3.4045043303\C
,-8.0029950361,-0.6340287334,-3.3898727896\C,-8.1462285794,-0.02415166
17,-1.9677620167\C,-9.3252216705,-0.8065103091,-1.3403583581\C,-10.237
1249519,-1.0697963533,-2.5823551873\C,-2.8003644279,3.4028582215,3.088
5164781\C,-3.0036103899,6.5702211835,3.5975456632\C,-3.8932025346,5.91
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0.7945603502\O,5.2079918638,0.1736202341,0.1917357359\O,3.6297095838,2
.3018267118,0.2425383644\O,-0.8901450976,3.0118126459,-1.2977098546\O,
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5,1.1400229398\H,-4.2716981048,-1.827610947,3.6339026812\H,-2.74662093
43,0.0567641473,3.1851498467\H,-0.3267684889,-2.4886148014,0.722266108
5\H,-1.0570431257,1.0217696884,1.9152217569\H,0.3788327099,0.067896677
3,2.2982654769\H,-0.9291318719,0.01606016,-0.462562242\H,0.6436507216,
-0.6341058316,-0.0016075815\H,1.3448704169,1.7585351304,0.6013292743\H
,-4.8741296591,-4.1170756055,3.3863919625\H,-3.7582114471,-5.288404399
,2.6889615271\H,-4.523954005,-4.8014707772,0.4211962246\H,-5.909663585
8,-5.1519376798,1.4333088706\H,-5.9956895843,-2.4700635527,1.743439199
\H,-0.8405142169,4.8743758595,4.2532336077\H,0.7189092907,6.2253301282
,2.1320315271\H,-0.0991884667,5.5239770077,0.0951800789\H,-2.463576272
8,3.7822967274,0.4303542157\H,0.09446275,4.0728353475,2.9997849092\H,-

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3942961214\H,-1.7321713666,5.8283178676,-0.4909493464\H,-3.8660740193,
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\H,-7.5560940522,-3.0934527995,-2.6299433848\H,-9.5422365383,-2.806999
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.556643323\H,-11.2834289277,-0.0274011226,-4.1649634202\H,3.0807720905
,0.882285662,-3.6807372828\H,4.7443266718,-2.0001023008,-0.8326861204\
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,-4.097757168\H,3.4277585461,-4.0634153029,-1.2861862109\H,5.005284728
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84,-3.8070563152\H,6.7297935531,1.7194092825,-0.1733716098\H,10.458731
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045925,-1.5137129142,0.7311817429\H,5.1979131217,-5.1480875913,2.30148
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255599,0.94781346\H,3.4877125101,-4.5022063357,3.8591481266\H,0.729224
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273\H,-0.9523600155,-3.0500867886,4.1558917677\H,-0.2280557824,-2.0750
428134,5.4480230218\H,-0.7344527095,-3.7265465628,5.78569123\H,11.7366
98644,1.0440534868,0.7204919492\H,10.3243768567,0.1072713926,1.1909700
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6598,-1.5196745517\H,12.8893155445,-0.4646595594,-1.5096085678\H,11.93
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83835721\H,-1.7954930872,1.2298713357,-2.3713540255\H,-3.1478728847,0.
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-4.2107890334\H,-2.1437965622,-1.5244782082,-3.6905504124\C,-5.0415371
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924557\C,3.9194855924,2.9308579118,1.5029373957\H,3.6950303348,2.23207
32985,2.3164527293\H,4.9863181251,3.1744677176,1.52535165\C,3.05826061
1,4.1743283019,1.5908363872\H,1.9969700499,3.9091650031,1.5374713644\H
,3.2880276287,4.8514550272,0.7641196342\H,3.2409259701,4.6962841655,2.
5346390236\C,3.0742950948,-1.1162101174,1.7810404395\H,3.6977148312,-1
.7464238284,1.1452252747\H,2.0910283132,-1.5863643127,1.8869275059\C,3
.7347971753,-0.8831817214,3.1214953029\H,3.1125784688,-0.2430326951,3.
7547148225\H,4.7106848775,-0.4089016268,2.9781924591\H,3.883951805,-1.
8399099356,3.6292478698\H,7.437278137,-3.2851066437,-1.7519203125\H,8.

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.6989943367\\Version=EM64L-G09RevA.02\State=1-A\HF=-6091.5786285\RMSD=
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Diels-Alder Product (n=m=2)

1\1\GINC-X150\Freq\RM062X\6-31G(d)\C94H146N2O18P2S4\JMH502\29-Oct-2012
\0\\#M062X/6-31G* INT(grid=ultrafine) Freq=noraman
maxdisk=402653184\\ch3-n2m2.freq\\0,1\C,-4.7989172307,-5.7562462934,-1
.4505135935\C,-3.6218260288,-4.9971273962,-0.8877331694\C,-2.388675639
,-4.986642524,-1.5449100549\C,-1.3470817722,-4.1784262087,-1.099529573
\C,-1.5135984655,-3.3340017274,0.0024852641\C,-2.7407620961,-3.3573892
042,0.6703304434\C,-3.7708366928,-4.1924715536,0.2465741746\C,-0.42885
77494,-2.379101563,0.4325833696\H,-2.2473461645,-5.6153819217,-2.42173
22861\H,-4.720561737,-4.2015310073,0.7796485469\H,-2.8958862959,-2.694
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6947261187,-1.9458280276,1.3976527092\H,0.5260603955,-2.905865264,0.56
87888735\H,-5.4565371163,-6.0901693826,-0.6449364725\H,-4.4488308556,-
6.6444326175,-1.9883945914\C,-5.6044779058,-4.8848096388,-2.4393009547
\H,-4.9451099905,-4.6144706246,-3.2731387822\H,-6.4294121321,-5.471898
1436,-2.8608080111\C,-6.1422578441,-3.5735396106,-1.8355153949\H,-5.34
81769956,-3.1756061217,-1.1882269209\C,-6.4553150224,-2.484850234,-2.8
654430856\H,-5.6862875235,-2.4737285913,-3.644383131\H,-7.4138922835,-
2.6587738065,-3.3618740286\P,-3.3096667289,0.8273997268,0.3613345344\O
,-2.3600819697,0.124170177,1.2523302932\O,-2.772579471,1.3763187402,-1
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,-4.8501945479,-0.3956014493,-1.9167839391\C,-6.5096872257,-1.13887853
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,-7.8749154421,5.7123928419,-0.9970964518\O,-7.6535463051,-0.050702059
,-3.99205934\H,-6.9060855276,-1.2624706189,-1.1393355424\H,-7.04489525
23,3.5759512207,0.543779711\H,-6.0323463416,4.8807649428,-3.1080276676
\H,-5.0147959948,2.9060549963,-1.5218749464\H,-6.0272990617,2.18316872
31,-3.4450408087\H,-8.9259061592,2.0355164897,-3.011827206\H,-6.704120
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ipole=-1.8486569,1.7741161,1.754966\PG=C01 [X(C94H146N2O18P2S4)]\@

3. Experimental characterization and calculation methodologies

3.1 Thermogravimetric analysis (TGA)

TGA measurements were performed utilizing a TGA Q5000 from TA-Instruments with ca. 5 mg of sample at temperatures ranging from ambient temperature up to 800°C. A 10°C per minute heating rate was employed.

3.2 Nuclear magnetic resonance (NMR) spectroscopy

The NMR debonding study was carried out using a DRX 500 spectrometer (Bruker, Germany) at 500 MHz. Deuterated DMSO was employed as the solvent and the measurements were collected at temperatures between room temperature and 120°C. Each spectrum was acquired after 4 minutes (^{1}H) and 6 minutes (^{31}P) of scanning time, in alternating order.

3.3 *Offline* size exclusion chromatography (SEC)

Molar mass distributions of polymeric samples were determined using a Polymer Laboratories PL–GPC 50 Plus Integrated System (Varian) comprised of an autosampler, a PLgel 5 µm bead-size guard column (50 × 7.5 mm), three PLgel 5 µm Mixed C columns (300 × 7.5 mm) (Agilent Technologies, USA), and a differential refractive index detector. THF was utilized as the eluent at 35°C with a flow rate of 1 mL min^{-1}. The SEC system was calibrated against linear poly(methyl methacrylate) (PMMA) standards with number average molecular weights ranging from 730 – 1.37 x 10^{6} g mol^{-1} (Polymer

Standards Service (PSS), Mainz, Germany) using the Mark-Houwink-Kuhn-Sakurada parameters for PMMA (K = 12.8 × 10^{-5} dL g^{-1} and α = 0.69) for universal calibration. All SEC calculations were performed relative to the PMMA standards and considering the Mark-Houwink-Kuhn-Sakurada parameters for PiBoA (K = 5 × 10^{-5} dL g^{-1} and α = 0.745) for universal calibration.[14]

3.3.1 Debonding assessed by number average molecular weight

Since DA-based polymerization is considered to be a step-growth polymerization process, the Carother's equation (equation (1)) can be applied to determine conversion from the DP_n as follows:

$$DP_n = \frac{1}{(1-X)} \qquad \text{Equation 1}$$

DP_n corresponds to degree of polymerization, which is equivalent to M_n/m, where M_n equals the number average molecular weight of a polymer sample and m equals the monomer average molecular weight. For all bis-cyclopentadiene poly(isobornyl acrylate-co-*n*butyl acrylate) (Cp_2-P(iBoA-*n*BA))-based DA polymers synthesized from the 1,4-phenylenebis(methylene)bis ((diethoxyphosphoryl)methanedithioformate) (P-di-linker) derived poly(isobornyl acrylate) (PiBoA) building blocks, the m is calculated by averaging the M_n of Cp_2-P(iBoA-*n*BA) with the M_n of the PiBoA. (The DP_n of the DA polymer derived from P-di-linker and Cp_2-P(iBoA-*n*BA), however, was calculated in an alternative manner; see below.) It should be noted at this time that the M_n values used for the PiBoAs and Cp_2-P(iBoA-*n*BA) were those measured after exposure to the same temperature for the same time as the experimental samples (see Section 7.3.2). X is the

conversion or, equivalently, the extent of bonding. Therefore, as presented previously by Zhou *et al.*[1], the percentage of bonding of monomers and, consequently, the percentage of debonded monomers in a DA or rDA polymer sample can be calculated from the M_n of that polymer according to the following rearranged Carother's equations:

$$\%\text{Bonding} = X\% = \left(1 - \frac{1}{DP_n}\right) \times 100 \qquad \text{Equation 2}$$

$$\%\text{Debonding} = 100 - X\% = \left(\frac{1}{DP_n}\right) \times 100 \qquad \text{Equation 3}$$

Given that the initial degree of polymerization (*i.e.*, percent bonding) resulting from each DA reaction obtained from a different size dienophile block was not equal and that it was suspected that the number of crosslinks present in a polymer chain could affect the debonding equilibrium point, only relative changes in the bonding of the DA polymers were compared. This method of comparing debonding was selected to isolate the effect of monomer chain length on the debonding equilibrium point. In other words, for every rDA reaction the debonding achieved was not taken as absolute, but rather as a fraction of change in bonding as compared to the initial bonding present in the DA starting polymer. For example, if only 60% bonding was achieved in a DA polymer and after a rDA reaction the polymer consisted of only 30% bonded monomers, this was interpreted as a polymer that underwent 50% decrease in bonding (*i.e.*, (initial bonding – final bonding)/ initial bonding)) as opposed to a polymer that was 70% debonded. Thus, the decrease in bonding was calculated as follows:

$$\%Decrease\ in\ Bonding\ = \left(1 - \frac{1-\frac{1}{DP_{\mathrm{nf}}}}{1-\frac{1}{DP_{\mathrm{ni}}}}\right) \times\ 100 \qquad \text{Equation 4}$$

where DP_{ni} equals DP_{n} after the DA reaction (*i.e.*, before the rDA reaction) and DP_{nf} is the DP_{n} after the rDA reaction.

As stated previously, a slightly different calculation methodology was used to determine the percent decrease in bonding for the P-di-linker+Cp_2-P(iBoA-*n*BA)-based DA polymer. Unfortunately, the lower detection limit of the *offline* SEC system was above the molecular weight of the P-di-linker, which means that in a 100% debonded state the lowest M_{n} value that could be measured by the SEC for the P-di-linker+Cp_2-P(iBoA-*n*BA)-based DA polymer would be the M_{n} value for the Cp_2-P(iBoA-*n*BA) block. Therefore, the DP_{n} of this polymer could not be calculated based on the average block size of P-di-linker and Cp_2-P(iBoA-*n*BA) (*i.e.*, ~7.2 kDa) because this low M_{n} value could never be achieved. However, assuming the average block size to be just the M_{n} value associated with Cp_2-P(iBoA-*n*BA) would also generate erroneous results because this would result in a great underestimation of the DP_{n} (up to 50%). The DP_{n} is equivalent to the number of monomers in a polymer chain; therefore, the next best method for determining the DP_{n} was to calculate the average number of total monomers (*i.e.*, Cp_2-P(iBoA-*n*BA) blocks + P-di-linker blocks) needed to form the polymer chain. Since the DA polymer is clearly a distribution of different size oligomers, it was assumed that the best approximation of the average number of total monomers per polymer was to determine the fraction of a smaller oligomer and a larger oligomer needed to reach the M_{n} of the polymer:

$$M_{nf} = x(a \times M_{n\text{-}Cp} + b \times MW_{P\text{-}di\text{-}linker}) + (1\text{-}x)((a+1) \times M_{n\text{-}Cp} + b \times MW_{P\text{-}di\text{-}linker}) \quad \text{Equation 5}$$

Or

$$M_{nf} = x(a \times M_{n\text{-}Cp} + b \times MW_{P\text{-}di\text{-}linker}) + (1\text{-}x)(a \times M_{n\text{-}Cp} + (b+1) \times MW_{P\text{-}di\text{-}linker}) \quad \text{Equation 6}$$

The known values are M_{nf}, which is the final M_n of the polymer (after the rDA reaction) in question, $M_{n\text{-}Cp}$, which is the M_n of Cp_2-P(iBoA-*n*BA) measured at the same temperature, time, and on the same day as the M_{nf}, and the $MW_{P\text{-}di\text{-}linker}$, which is 530.62 g mol^{-1}. Therefore, the equation is solved for x, which is equal to the fraction of small oligomers that make up a polymer with the molecular weight M_{nf}. Values for a and b must be selected in order to satisfy two conditions: (*i*) the total number of monomers results in an M_n that is smaller than M_{nf}, but larger than M_{nf} when one supplementary monomer is added to the M_n and (*ii*) |a - b| must always be 1 or 0. Also, if b > a, then Equation (5) must be utilized and if a > b, then Equation (6) must be employed. When there are 2 possible a, b assignments, then both are considered separately and the final DP_n is an average of the DP_n found for each scenario. Finally, for each a, b assignment/scenario the fraction of monomers in the small oligomer was then added to the fraction of monomers from the large oligomer to give the DP_n, as shown below:

$$DP_n = x(a + b) + (1 - x)(a + 1 + b) \quad \text{Equation 7}$$

An example calculation for the P-di-linker+Cp_2-P(iBoA-*n*BA)-based DA polymer with an M_n = 28,500 Da is presented. Given $M_{n\text{-}Cp}$ = 13,800 Da and $MW_{P\text{-}di\text{-}linker}$ = 530.6 g mol^{-1}, Equation (5) is employed where a and b have been selected to be 1 and 2, respectively:

$$28{,}500 = x(1 \times 13{,}800 + 2 \times 530.6) + (1 - x)(2 \times 13{,}800 + 2 \times 530.6)$$

Therefore, x is 0.014, which when substituted into Equation (7) gives a DP_n = 3.99. When the DP_n value of 3.99 is substituted into Equation (2), the percentage of bonding in this DA polymer is calculated to be ~75%. For this example no other combination of a and b could be selected to satisfy either Equation (5) or (6).

3.4 *Online* temperature dependent high temperature size exclusion chromatography (HT SEC)

Two Agilent HT SEC instruments (Polymer Laboratories, UK) were employed for the *online* temperature dependent characterization of the rDA properties of the DA polymers. All components of both setups, except the solvent and waste reservoirs, were integrated into an oven that could be heated as high as ~200°C (see Figure S3). For our purposes the HT SEC systems were used in the temperature range of 80°C to 150°C.

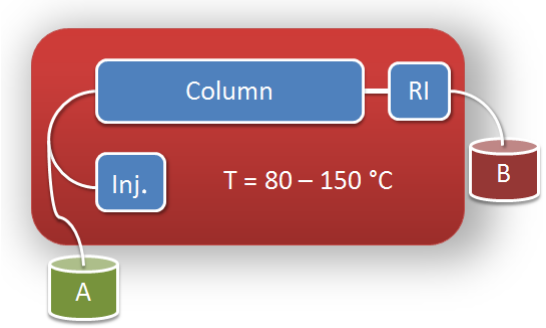


Figure S3. Schematic of the high temperature SEC system setup (A = solvent reservoir, Inj. = injection unit, RI = Refractive index detector, B = solvent waste).

The online SEC evaluation of the molar mass distributions that result following the rDA reaction of the IPDI-SA+P-di-linker DA polymer, P(IS-PL)1, at elevated temperatures was performed utilizing a PL GPC-210 system equipped with a ResiPore (3 μm) column (Agilent Technologies, USA) and a differential refractive index detector. The system employed DMSO as the eluent, the flow rate of which was maintained at 0.7 mL min^{-1}. DMSO was selected as the eluent to prevent the sample aggregation that occurs in 1,2,4-Trichlorobenzene (TCB). Each sample was prepared at a 3.75-4 mg mL^{-1} concentration and 100 μL was allowed to equilibrate to the desired temperature for the desired time in the injection loop prior to being injected into the column for analysis. The system was calibrated against poly(2-vinylpyridine) (PVP) standards (1,050 – 297,000 g mol^{-1}) (Polymer Standards Service, Germany). Number average molecular weight (M_n), weight average molecular weight (M_w), and molar mass dispersity ($Đ_M$) were calculated relative to PVP standards. PVP standards were utilized instead of poly(styrene) (PS) standards because it was believed that PVP would interact with the column in a fashion more similar to the manner in which the IPDI-SA+P-di-linker DA polymer interacts with

the column. This assumption was based on the fact that both polymers have similar solubility in DMSO and possess amine groups, whereas PS does not.

The remainder of the IPDI-SA-based DA polymers, **P(IS-PL)2-4,** were characterized on a PL GPC-220 system employing TCB as the eluent with a flow rate of 0.6-1.0 mL min^{-1}. This system was equipped with two PLGel Mixed-D (5 μm) columns (Agilent Technologies, USA), a differential refractive index detector, and an autosampler. Each sample (3-4 mg mL^{-1}) was injected 200 μL at a time from an autosampler. The Cp_2-P(iBoA-*n*BA)-based DA polymers, **P(Cp-PL)1** and **P(Cp-PL)5-7,** were also characterized on the PL GPC-220 system described above; however, a PLGel Mixed-BLS (10μm) column (Agilent Technologies, USA) and a PureGPC-ORG (5 μm) column (WGE Dr. Bures, Germany) were used in place of the PLGel Mixed-D columns. Polymer samples were characterized at a 2-3 mg mL^{-1} concentration. The PL GPC-220 system was always calibrated against PS standards (580 – 210,500 g mol^{-1}) (Polymer Laboratories, UK). All SEC calculations were performed relative to the PS standards.

All characterized DA polymers and precursors were subjected to the desired temperature (80-140°C) for times ranging from 0 to 300 minutes prior to injection. Thus, the progress of the rDA reaction could be observed online at different times and temperatures. In all cases, the HT SEC systems were calibrated every day at the temperature that was utilized for the experiments prior to performing the experimental characterization. The acquired chromatograms were analyzed either by calculating the number average molecular weight, relative to a standard, or by peak deconvolution.

3.4.1 Debonding assessed by number average molecular weight

The calculation methodology that was utilized to determine the bonding/debonding percentages from the M_n values obtained from the *offline* SEC characterization of the Cp_2-P(iBoA-*n*BA)-based DA polymer (see Section 3.3.1, Equation (4)) was also applied to the evaluation of the data acquired from the *online* HT SEC characterization of the IPDI-SA-based DA polymers. One small alteration that was made to the calculations, however, was that the average monomer molecular weight value (*m*) employed in the calculations was not the average of the PiBoA block and IPDI-SA, but rather was just the M_n value of the PiBoA block. The reason for this was equivalent to the reason for which Equations (5), (6), and (7) were applied to the calculation of the DP_n of the P-di-linker+Cp_2-P(iBoA-*n*BA)-based polymer. The molecular weight of IPDI-SA was under the lower limit of detection of the HT SEC. Therefore, at 100% debonding the smallest molecular weight that could be detected would be that of the PiBoA and not that of the average of the PiBoA and IPDI-SA. Instead of applying Equations 5, 6, and 7 to calculate the DP_n of the IPDI-SA-based polymers from the measured M_n, which would require an extensive quantity of tedious calculations given all the data points for the kinetic measurements, *m* was simply assumed to be the M_n of PiBoA. Although the debonding values calculated would be inaccurate, likely higher, than the actual values (except in the case of 100% debonding), the effect would be the same on all IPDI-SA+PiBoA-based DA polymers, if the same calculation methodology was consistently employed. Therefore, the relative differences between the debonding values from sample to sample, time to time, and temperature to temperature would result in the same trend than if Equations (5), (6), and (7) had been applied to the data. One small caveat to this

calculation approach was that it could not be applied to the P-di-linker+IPDI-SA polymer because both monomers were below the HT SEC detection limit. For the evaluation of data from the P-di-linker+IPDI-SA system, the original equation for calculating DP_n, where *m* equals the average molecular weight of P-di-linker and IPDI-SA, was employed. Unfortunately, employing two different calculation methodologies for the evaluation of the rDA properties of the library of IPDI-SA-based polymers means that the debonding values obtained for the IPDI-SA+PiBoA polymers are not directly comparable to the values obtained for the IPDI-SA+P-di-linker polymer; the former values are likely higher than they should be.

3.4.2 Debonding assessed by chromatogram deconvolution

The results of the HT SEC characterization of a small subset of the Cp_2-P(iBoA-*n*BA)-based DA polymer library were assessed both by employing the calculation methodology presented in Section 3.3.1 (used to evaluate the *Offline* SEC results) and by deconvoluting the HT SEC chromatograms. Although simply employing the former methodology would have been more consistent, this would have required a separate PiBoA and Cp_2-P(iBoA-*n*BA) control measurement for every time and temperature studied. However, these control samples could not be analyzed in tandem with the experimental samples because of limitations of the HT SEC system and the calibration method employed at different temperatures. Consequently, a smaller subset of controls was performed in which each PiBoA and the Cp_2-P(iBoA-*n*BA) was characterized by HT SEC at each elevated temperature, but only for a short time (see Table S8). Unfortunately, given that it has been observed that there is a slight decrease in the M_n

values associated with the PiBoAs after heating (especially above 100°C) over extended time periods, these controls were likely not adequate enough. This is further supported by the fact that over 100% debonding is calculated using the M_n-based calculation methodology, which could be explained by the rDA reaction M_n being lower than the control average monomer molecular weight because the PiBoA control M_n values were too high. Due to the unreliability of this approach peak deconvolution was employed to analyze the data instead.

Peak deconvolution is often used to separate overlapping peaks by describing the single peaks with adequate peak functions and adjusting their parameters in order to fit the sum of the functions to the experimentally acquired curve. In the literature, reviews and evaluations of the quality of different functions for different applications can be found.[15-17] The chromatograms collected from the HT SEC analysis of the Cp_2-P(iBoA-*n*BA)-based DA polymers were evaluated using the relatively simple Gauss distribution function shown in equation 8.

$$y = y_0 + \frac{A}{w\sqrt{\pi/2}} e^{-2\frac{(x-x_c)^2}{w^2}} \qquad \text{Equation 8}$$

where y_0 is an offset value, A is the peak area, w is the width of the peak and x_c is the position of its center. The parameters x_c and w are specific for the single components (they correspond to elution time and molar mass dispersity) and can be determined from chromatograms of the single components so that in the mixture, the only parameter that has to be optimized is the peak area A, which gives the amount of the polymer.

The procedure for the calculation of the content of Cp_2-P(iBoA-*n*BA) is as follows:

a) Acquire the chromatograms of the pure PiBoAs and Cp_2-P(iBoA-*n*BA) for a known concentration.

b) Fit the chromatograms with Gauss functions. Since the peaks are asymmetrical, two overlaid Gauss functions were used for the PiBoA building blocks and three for the Cp_2-P(iBoA-*n*BA), which additionally showed a high molecular weight shoulder. This gives the peak center and width information for these components plus a peak area – concentration correlation.

c) Acquire the chromatograms of the Cp_2-P(iBoA-*n*BA)-based DA polymers at the desired temperature and reaction time.

d) Use the peak functions found in step (b) plus an additional "polymer" Gauss function to fit the chromatogram. The latter describes the unknown part of the DA polymer. In contrast to the PiBoA and Cp_2-P(iBoA-*n*BA) components, the parameters for peak center and width corresponding to DA polymer cannot be predetermined. Therefore, these parameters are selected in order to give the best fit for the chromatogram. The only criterion that must be satisfied is that the peak center must occur at an earlier elution time than the peak center for the PiBoA peak.

e) Determine the concentration of Cp_2-P(iBoA-*n*BA) from the Cp_2-P(iBoA-*n*BA) peak area by employing the concentration to peak area correlation determined in step (b).

In order to set a relative 0% debonding value and 100% debonding value, the Cp_2-P(iBoA-*n*BA) concentration was determined for the DA polymer at 25°C (*i.e.*, prior to rDA reaction) and after heating at 120°C for 5 h, respectively. The 'Normalized % Cp_2P(iBoA*n*BA)' value is then calculated with Equation (9).

$$Normalized\ \%Cp_2P(iBoAnBA) = \left(\frac{Cp_2P(iBoAnBA)_T - Cp_2P(iBoAnBA)_0}{Cp_2P(iBoAnBA)_{max} - Cp_2P(iBoAnBA)_0}\right) \times 100$$

Equation 9

$Cp_2P(iBoAnBA)_T$ corresponds to the content of Cp_2-P(iBoA-*n*BA) in the DA polymer after heating at temperature T (for 5 h) and $Cp_2P(iBoAnBA)_0$ equals the initial content of Cp_2-P(iBoA-*n*BA) in the DA polymer, prior to heating (at 25°C). $Cp_2P(iBoAnBA)_{max}$ is established as the Cp_2-P(iBoA-*n*BA) content in the DA polymer after heating at 120°C for 5 h because qualitative assessment of the corresponding chromatogram suggested that 100% debonding had been achieved. Hence, the normalized %Cp_2-P(iBoA-*n*BA) values should correspond directly to the decrease in bonding. Therefore, the data has been plotted in terms of normalized %Cp_2-P(iBoA-*n*BA), but has been referred to as 'decrease in bonding' in Figure 5a of the Manuscript.

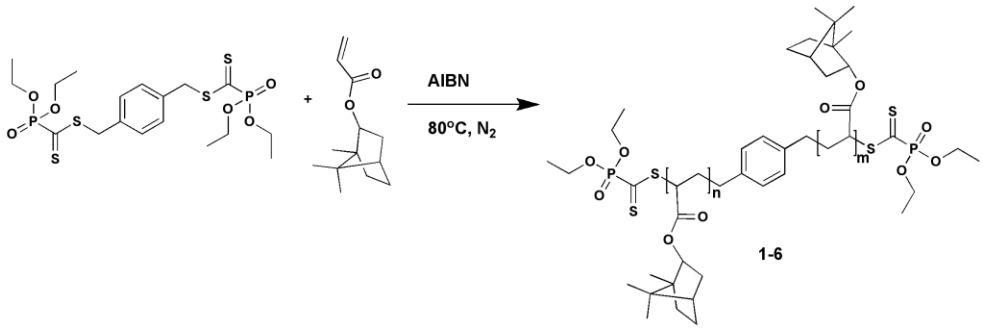
3.5 SEC (25°C) utilized for *online* HT SEC calculations

Given that the HT SEC measurements were performed at a different institution and that the M_n values obtained from the HT SEC instrument were, for the most part, calculated with respect to PS standards, all building blocks and DA polymers were recharacterized by a SEC located at the same institution as where the HT SEC was located. In addition, the absolute molecular weights of the DA polymers and building blocks were determined using this same SEC, which was coupled to a static light scattering detector. This characterization was performed at 25°C in THF (stabilized with 0.025 % BHT), with a flow rate of 1 mL min^{-1}, on a SEC (series 1200, Agilent, US) equipped with a PLGel 10 µm Mixed-C column (Polymer Laboratories, UK), a ETA 2020 refractive index detector,

a viscosity detector (WGE Dr. Bures, Germany), as well as a three angle static light scattering detector (WYATT MiniDawn TriStar, Wyatt Techn., US). The SEC system was calibrated against linear PS standards with M_n values ranging from 580-210,500 g mol^{-1} (Polymer Laboratories, UK). All SEC calculations were performed relative to the PS standards. Light scattering was carried out at 45°, 90°, and 135°.

4. Synthesis

4.1 Reversible addition-fragmentation chain-transfer (RAFT) polymerization of poly(isobornyl acrylate) (PiBoA) (1-6)



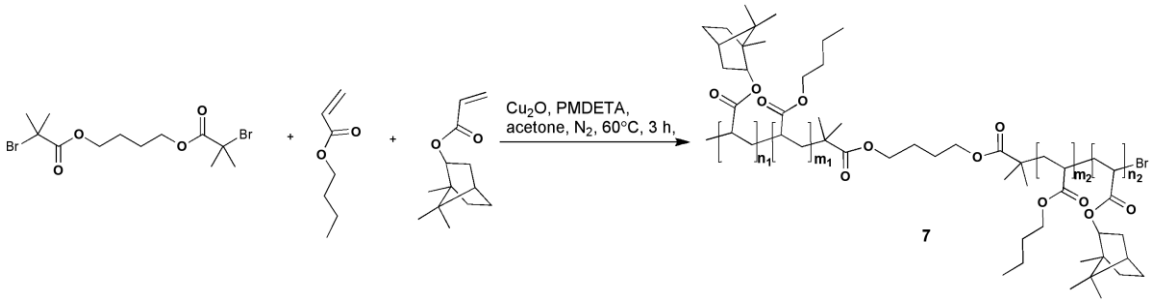
Scheme S1. Reversible addition-fragmentation chain-transfer (RAFT) polymerization of isobornyl acrylate mediated by P-di-linker in the presence of AIBN.

The synthesis of a library of difunctional dienophiles was accomplished by reversible addition-fragmentation chain-transfer (RAFT) polymerization of isobornyl acrylate (iBoA) in the presence of P-di-linker and 2-2'-azoisobutyronitrile (AIBN) at 80°C under inert atmosphere (see Scheme S1). Depending on the targeted M_n, the equivalents of P-di-linker to iBoA to AIBN was either 1 : 350 : 0.2 or 1 : 800 : 0.2. By employing a near-infrared probe to monitor the disappearance of iBoA and, therefore, the extent of conversion, the number average molecular weight (M_n) and, consequently, the chain

length of the di-functional dienophile end-capped poly(isobornyl acrylate) (PiBoA) was varied.

A typical protocol for the RAFT polymerization is as follows. iBoA (165 g, 792.12 mmol) was added to P-di-linker (1.20 mg, 2.26 mmol) and AIBN (74.2 mg, 0.45 mmol) in a flask. The solution was mixed vigorously until P-di-linker and AIBN completely dissolved. The solution was subjected to 4 freeze-pump-thaw cycles to deoxygenate it. Under nitrogen and in the presence of a near infrared (NIR) probe the solution was heated at 80°C until the approximate polymer conversion that was desired was achieved (based on NIR spectroscopy). Reaction times varied from 3-6 h depending on the reaction conditions and targeted conversion (*i.e.*, ~5-20%). The reaction was terminated by exposing the solution to air and precipitating the PiBoA in cold methanol. The PiBoA was redissolved in a minimal amount of chloroform and reprecipiated in methanol two to three more times to remove as much of the iBoA as possible. PiBoA1, PiBoA2, PiBoA3, PiBoA4, PiBoA5, and PiBoA6 were isolated, each of which had an M_n of 6.1, 10.8, 18.9, 20.2, 31.5, and 41.4 kDa, respectively.

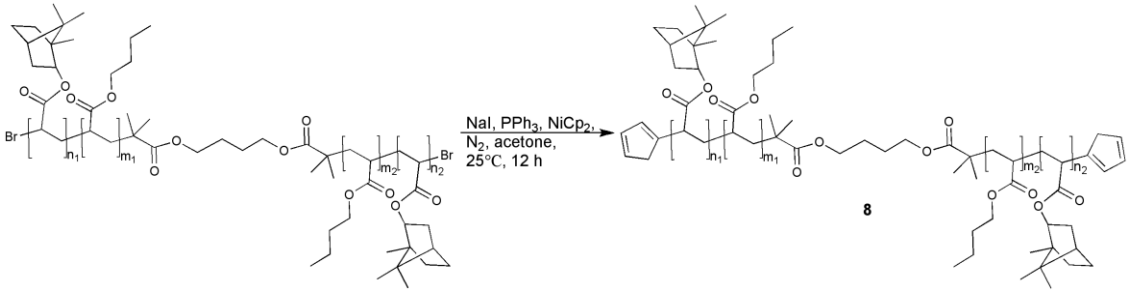
4.2 Synthesis of Br-functionalized poly(isobornyl acrylate-co-*n*butyl acrylate) (7)



Scheme S2. Atom transfer radical polymerization (ATRP) of *n*-butyl acrylate and isobornyl acrylate from the initiator 1,4-bis(bromo isobutyryloxy)butane in the presence of copper(I)oxide and N,N,N',N",N''-pentamethyldiethylenetriamine (PMDETA).

n-Butyl acrylate (*n*BA) (50 g, 0.39 mol), isobornyl acrylate (100 g, 0.48 mol), 1,4-bis(bromo isobutyryloxy)butane (5.8 g, 17 mmol), copper(I)oxide (0.75 g, 5 mmol), and 2,2'-PMDETA (1.82 g, 10 mmol) were placed in a 1 L three-neck round bottom flask equipped with a magnetic stirrer, a nitrogen inlet and a reflux condenser. Acetone (150 mL) was added to fully dissolve the reagents. The reaction mixture was deoxygenated by purging with nitrogen for 40 min. Next, the mixture was heated at 60°C for 3 h. The reaction was ended by cooling the solution to room temperature and bubbling air through the mixture for 10 min. The copper catalyst was removed by adding zinc dust (2 g) and acetic acid (1 mL) as described elsewhere.[18] The bromo-terminated polymer **7** was isolated by precipitation in methanol and subsequent drying in a vacuum oven.

4.3 Synthesis of Cp-functionalized poly(isobornyl acrylate-co-*n*butyl acrylate) (Cp_2-P(iBoA-*n*BA)) (8)



Scheme S3. Synthesis of bis-cyclopentadiene end-capped poly(isobornyl acrylate-co-*n*butyl acrylate) (P(iBoA-*n*BA)) from dibromine-functionalized P(iBoA-*n*BA) in the presence of nickelocene ($NiCp_2$).

Under nitrogen polymer **7** (18 g, ~2 mmol), sodium iodide (1.7 g, 12 mmol), triphenyl phosphine (0.9 g, 4 mmol), and nickelocene (0.7 g, 4 mmol) were placed in a 500 mL three-necked round bottom flask equipped with a magnetic stirrer, a nitrogen inlet, and a dropping funnel. Acetone (60 mL) was added, resulting in a greenish solution. The

solution was stirred at ambient temperature for 12 h, during which time the solution color changed from green to purple. Next, the solution was passed through a short alumina (basic) column to remove the solid. The eluent containing the Cp-terminated polymer (Cp_2-P(iBoA-*n*BA)) **8** was concentrated and then precipitated twice from acetone in cold ethanol by the addition of 50% water. The precipitate was collected and dried to give an off-white solid.

4.4 DA polymerization of P-di-linker/PiBoA block with Cp_2-P(iBoA-*n*BA) (P(Cp-PL)1-7) or IPDI-SA (P(IS-PL)1-4)

The DA step-growth polymerization was performed by adding 10.2 μL of a solution of $ZnCl_2$ in THF (0.125 mg mL^{-1}) to a solution of Cp_2-P(iBoA-*n*BA) (0.0086 mmol) and dienophile di-linker (0.0086 mmol) in 289.8 μL toluene. The reaction mixture was subsequently heated at 50°C for 20-24 h. The resulting viscous DA polymer was diluted in 2 mL of chloroform, after which the solution was washed twice with 2 mL of water to remove the $ZnCl_2$. Following drying in a vacuum oven at ambient temperature overnight, the DA products were characterized by SEC (Supplementary Section 3.3) at a concentration of ~2 mg mL^{-1}. In this way, DA polymers P(Cp-PL)1-7 were generated from P-di-linker, PiBoA1, PiBoA2, PiBoA3, PiBoA4, PiBoA5, and PiBoA6, respectively (Supplementary Table S2). Similarly, DA polymers P(IS-PL)1-4 were generated from P-di-linker, PiBoA4, PiBoA5, and PiBoA6, respectively (Supplementary Table S6).

5. TGA characterization of building blocks and DA polymers

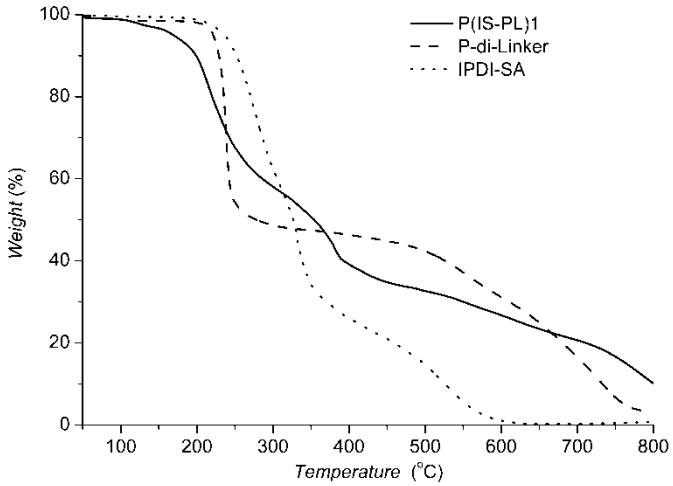


Figure S4. TGA curves of P(IS-PL)1 DA polymer, P-di-linker, and IPDI-SA. Weight loss occurring between 40 and 800°C for a temperature scan rate of 10°C per minute is depicted.

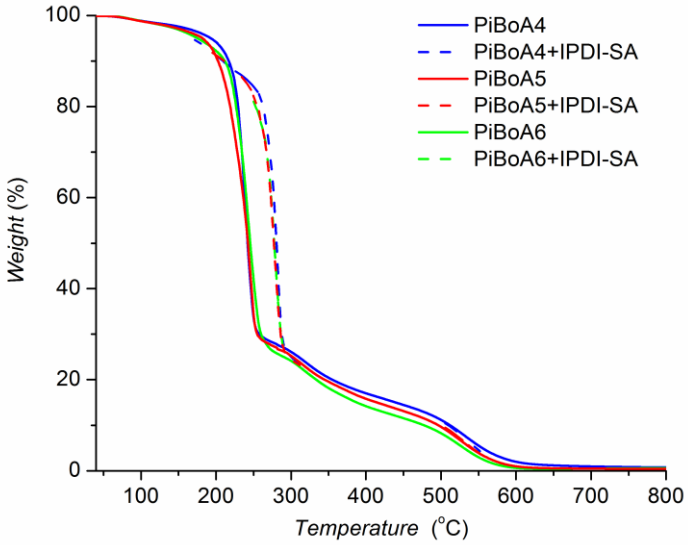


Figure S5. TGA curves of PiBoA4, P(IS-PL)2 (*i.e.*, PiBoA4+IPDI-SA) polymer, PiBoA5, P(IS-PL)3 (*i.e.*, PiBoA5+IPDI-SA) polymer, PiBoA6, and P(IS-PL)4 (*i.e.*, PiBoA6+IPDI-SA) polymer. Weight loss occurring between 40 and 800°C for a temperature scan rate of 10°C per minute is depicted. The weight loss observed to occur under 200°C is attributed to the evaporation of remaining iBoA.

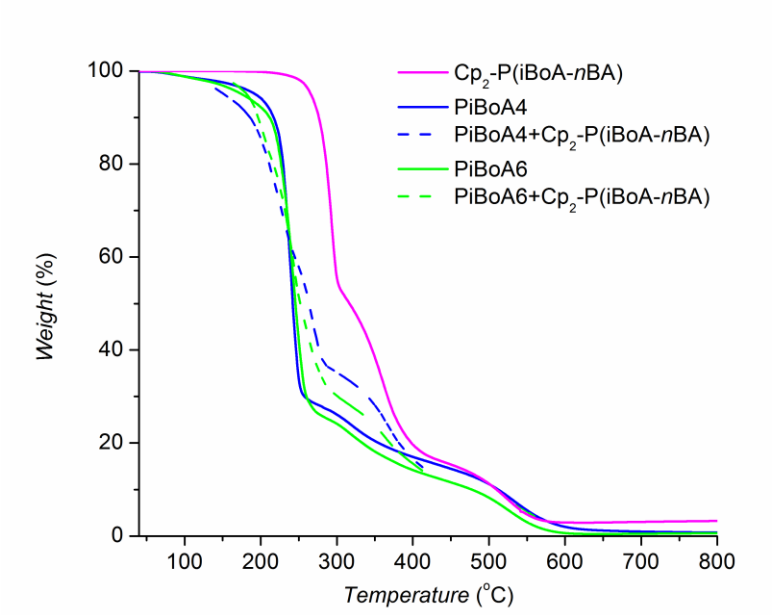


Figure S6. TGA curves of Cp_2-P(iBoA-*n*BA), PiBoA4, P(Cp-PL)5 (*i.e.*, PiBoA4+Cp_2-P(iBoA-*n*BA)) DA polymer, PiBoA6, and P(Cp-PL)7 (*i.e.*, PiBoA6+Cp_2-P(iBoA-*n*BA)) DA polymer. Weight loss occurring between 40 and 800°C for a temperature scan rate of 10°C per minute is depicted. The weight loss observed to occur under 200°C is attributed to the evaporation of remaining isobornyl acrylate.

6. NMR characterization of the debonding of the P(IS-PL)1 system

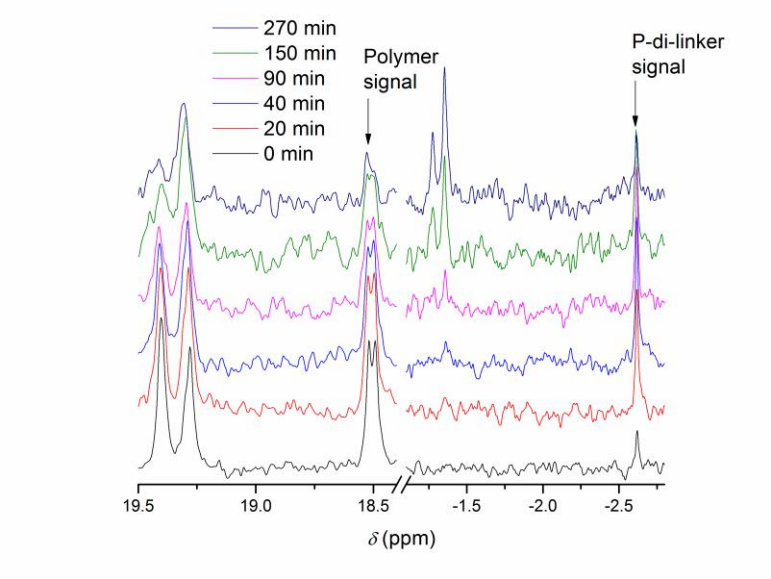


Figure S7. ^{31}P NMR spectra of the P(IS-PL)1 DA polymer (based on IPDI-SA and P-di-linker) after 20, 40, 90, 150, 270 min at 120°C. The resonance signal associated the P-di-linker monomer, at -2.62 ppm, increases in intensity, while the intensity of the resonance signals above 15 ppm, likely associated with the polymer, decrease in the first 90 min. However, by 150 min at 120°C the signal at -2.62 ppm begins to decrease, while a resonance signal at ~1 ppm begins to increase. This trend could be attributed to monomer degradation, for instance the phosphonate groups may undergo hydrolysis in the presence of trace water in DMSO at high temperatures.

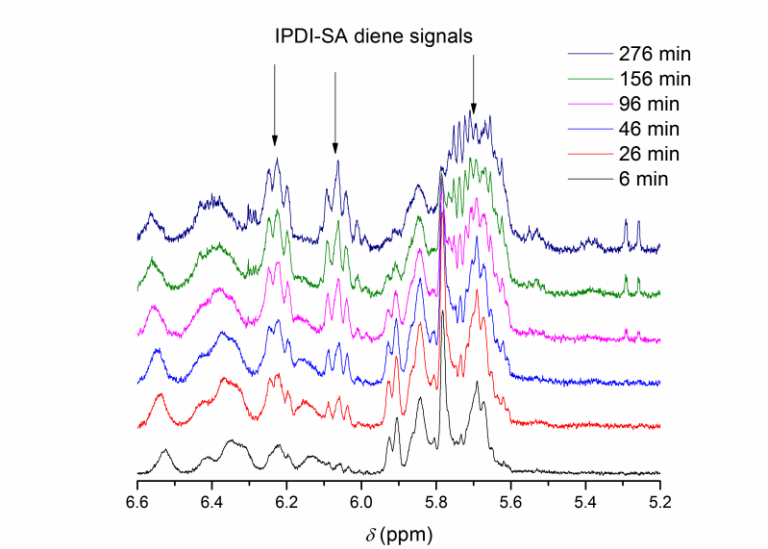


Figure S8. ^{1}H NMR spectra of the P(IS-PL)1 DA polymer (based on IPDI-SA and P-di-linker) after 6, 26, 46, 96, 156, and 276 min at 120°C. The increase in the intensity of the resonance signals at 6.22, 6.05, and 5.7 ppm and the decrease in the intensity of the resonance signal at 5.78 ppm over time are correlated with the regeneration of the protons associated with the diene in IPDI-SA and the disappearance of the protons associated with the double bond of the cycloadduct, respectively.

7. *Offline* SEC characterization of the P(Cp-PL) DA polymer systems

7.1 PiBoA and Cp_2-P(iBoA-*n*BA)) building blocks

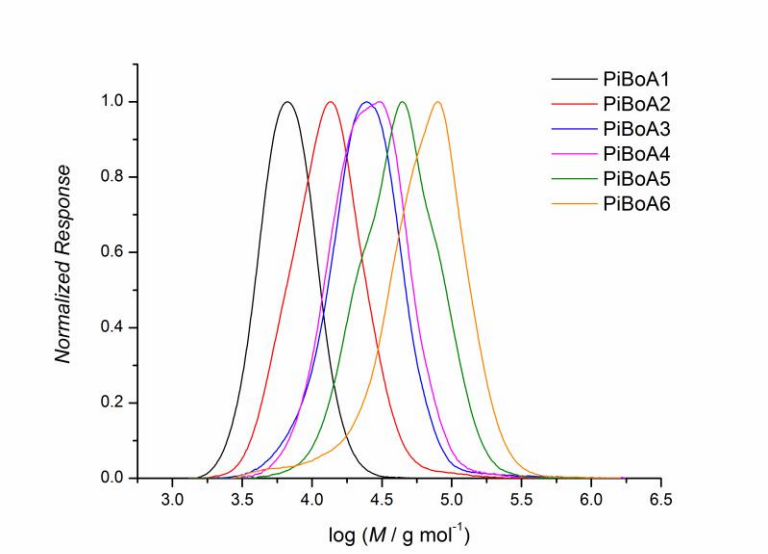


Figure S9. SEC traces of the PiBoA building blocks.

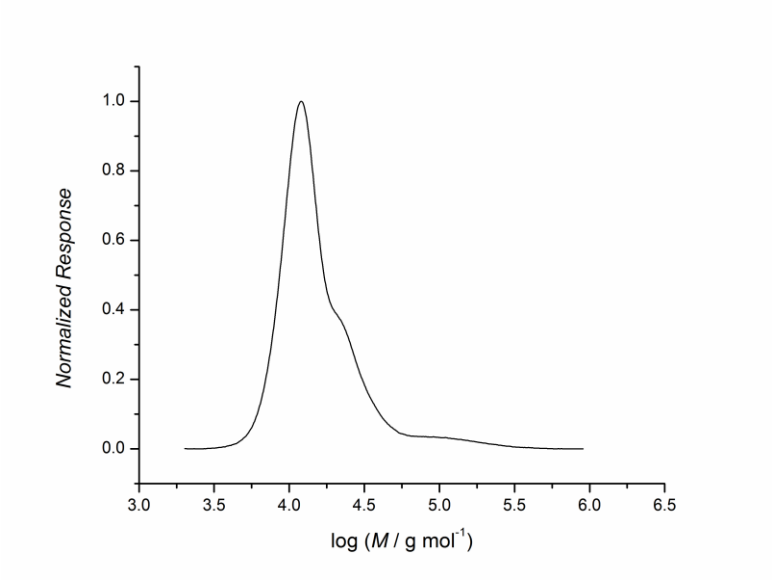


Figure S10. SEC trace of the Cp_2-P(iBoA-*n*BA) building block. The small high molecular weight shoulders likely correspond to the self-dimerization of cyclopentadiene, which is typical of cyclopentadiene functionalize polymers.

Table S1. A summary of all polymer building blocks synthesized and their respective M_n, M_w, and $Đ_M$ values, as determined by refractive index detection. Molecular weight values are calculated with respect to poly(methyl methacrylate) standards and recalibrated according to poly(isobornyl acrylate) Mark-Houwink constants.

Polymer	M_n (kDa)	M_w (kDa)	$Đ_M$
PiBoA1	6.1	7.6	1.23
PiBoA2	10.8	15.3	1.42
PiBoA3	18.9	28.2	1.49
PiBoA4	20.2	29.4	1.45
PiBoA5	31.5	47.9	1.52
PiBoA6	41.4	73.5	1.77
Cp_2-P(iBoA-*n*BA)	13.9	20.7	1.49

7.2 DA polymers

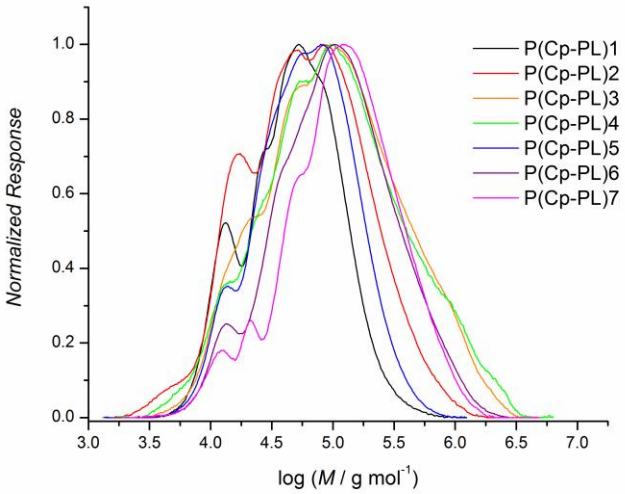


Figure S11. Chromatograms for the P(Cp-PL) DA polymers, synthesized at 50°C for 24 h, as measured by the *offline* SEC instrument (at 35°C). The difunctional dienophile block utilized in the DA reaction is indicated in the legend.

Table S2. A summary of all P(Cp-PL) DA products (formed from Cp_2-P(iBoA-*n*BA) and P-di-linker/PiBoA) and their respective M_n, M_w, and $Đ_M$ values. Molecular weight values are calculated with respect to poly(methyl methacrylate) standards and recalibrated according to poly(isobornyl acrylate) Mark-Houwink constants.

Polymer	Dienophile	M_n (kDa)	M_w (kDa)	$Đ_M$	Bonding (%)
P(Cp-PL)1	P-di-linker	28.5	58.9	2.07	72.2*
P(Cp-PL)2	PiBoA1	27.7	89.8	3.25	63.7
P(Cp-PL)3	PiBoA2	40.3	183.9	4.57	69.3
P(Cp-PL)4	PiBoA3	37.9	203.8	5.38	56.7
P(Cp-PL)5	PiBoA4	34.6	75.8	2.19	50.6
P(Cp-PL)6	PiBoA5	47.4	155.0	3.27	52.1
P(Cp-PL)7	PiBoA6	51.3	163.6	3.19	42.4

*Different calculation method used, see Section 3.3.1.

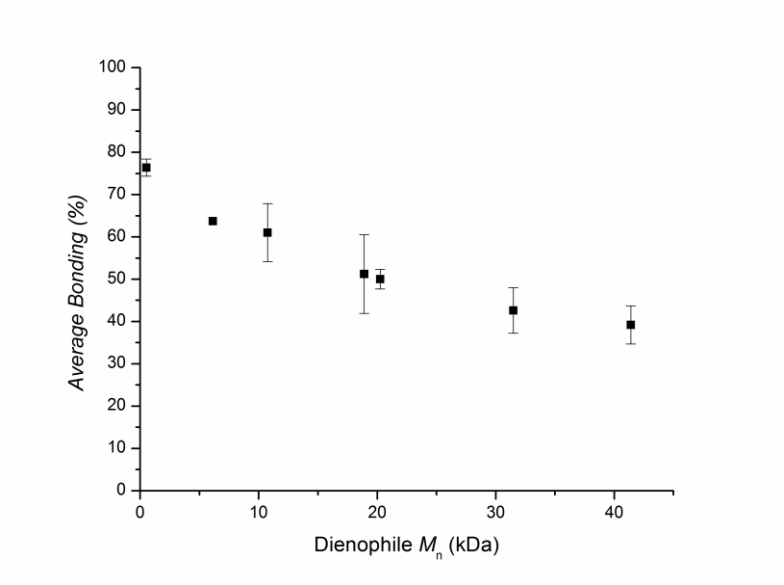


Figure S12. The bonding percentage achieved in the DA polymerization with Cp_2-P(iBoA-*n*BA) decreases as the size of the dienophile (*i.e.*, PiBoA) is increased. Most DA reactions were performed 3-4 times. Therefore, the average bonding percentage and the corresponding standard deviation for these reactions are plotted.

7.3 rDA properties of the P(Cp-PL) DA polymers

7.3.1 rDA kinetic study

The kinetics the rDA reaction for the DA polymer P(Cp-PL)5, composed of PiBoA4 and Cp_2-P(iBoA-*n*BA), were evaluated in toluene at a concentration of 10 mg mL^{-1} (~0.3 mM) for times ranging from 0-20 h at 160°C. Equilibrium appeared to be reached after 5-10 h (Figure S14). Consequently, all future rDA reactions to be analyzed by the *offline* SEC were conducted for 20 to 24 h to ensure that regardless of the polymer and temperature that the equilibrium point would be reached prior to characterization.

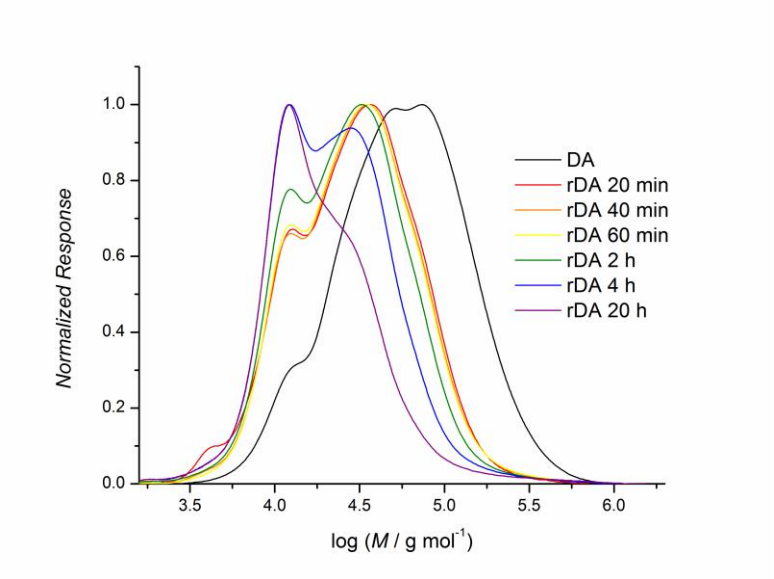


Figure S13. SEC traces depicting the molecular weight distributions associated with the rDA reactions of the P(Cp-PL)5 DA polymer at 160°C after 20 min, 40 min, 1 hr, 2, hr, 4 hr, and 20 hr. The molecular weight distributions shift to lower molecular weight values as time progresses, signifying the progression of the rDA reaction.

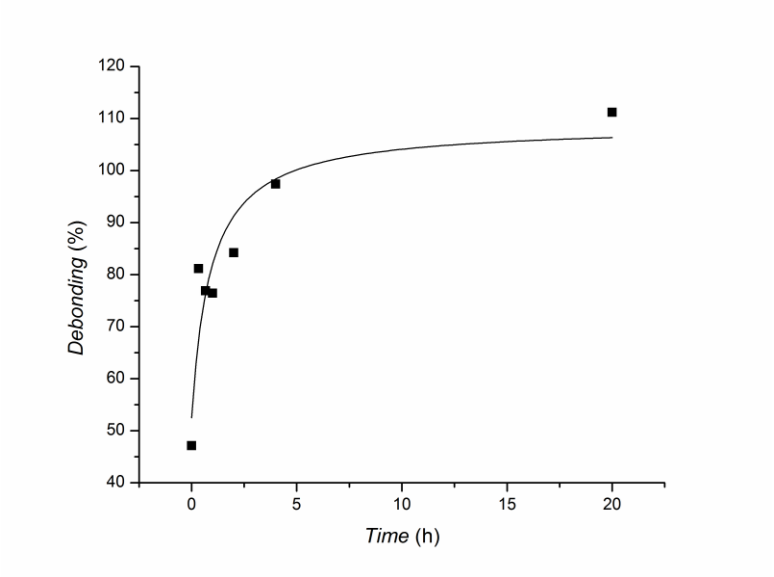


Figure S14. The kinetics of the rDA reaction of the DA polymer P(Cp-PL)5 at 160°C over 20 h. Debonding values were determined from the M_n obtained from SEC (see Figure S13) and Equation (3).

7.3.2 Building block temperature control study

In addition to implementing the experimental protocol, control assays were performed in which solutions of the building blocks were subjected to the same exact conditions as employed for the rDA reaction (Figure 3a in the Manuscript). Averaging the M_n value of the control Cp_2-P(iBoA-*n*BA) block with that of the relevant control PiBoA block permitted the determination of the apparent average block M_n at a given temperature (Table S3), which could be considered the smallest possible M_n value obtained for the rDA reaction of the DA product corresponding to the PiBoA block in question, assuming 100% debonding. The validity of the assumption that the M_n values of each building block of a DA polymer could simply be averaged to obtain the apparent M_n value that would be measured if the blocks coexisted in solution with no DA product formed was assessed for several block combinations and at several temperatures (see Table S3). In all cases the theoretical average block M_n value and the experimental block mixture M_n value coincided with, on average, 3% error, but always less than 8% error. Thus, comparing the rDA M_n of a DA polymer to the control average block M_n permitted a more realistic calculation of the percent debonding achieved. To minimize any distortion of the data that could arise from day to day variability in SEC, the rDA reactions of all DA polymers performed at one temperature and the corresponding controls were always performed on the same day.

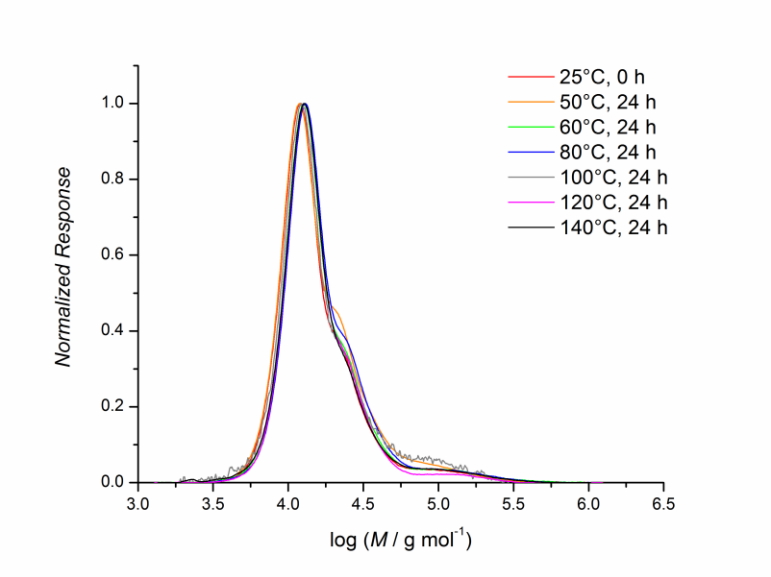


Figure S15. SEC traces of Cp_2-P(iBoA-*n*BA) after heating at temperatures ranging from 50°C to 140°C for 24 h compared to the chromatogram of Cp_2-P(iBoA-*n*BA) without any heating (*i.e.*, 25°C, 0 h).

Table S3. Building block temperature control study. The M_n, M_w, and $Đ_M$ values for the PiBoA building blocks, the M_n values for Cp_2-P(iBoA-*n*BA), and the corresponding average block M_n values are given for 25, 60, 80, 100, 120, and 140°C. Molecular weight values are calculated with respect to poly(methyl methacrylate) standards and recalibrated according to poly(isobornyl acrylate) Mark-Houwink constants.

PiBoA	Temp. (°C)	M_n (kDa)	M_w (kDa)	$Đ_M$	Cp_2-P(iBoA-*n*BA) M_n (kDa)	Theoretical Avg. block M_n (kDa)	Experimental Avg. block M_n^* (kDa)
PiBoA1	25	6.1	7.6	1.2	13.9	10.0	--
	60	6.1	7.5	1.2	13.8	9.9	10.6
	80	6.0	7.5	1.2	14.1	10.1	10.1
	100	5.7	7.0	1.2	13.2	9.5	9.9
	120	6.0	7.6	1.3	13.5	9.7	--
PiBoA2	25	10.8	15.3	1.4	13.9	12.3	12.3
	60	10.7	14.8	1.4	13.8	12.2	12.1
	80	10.5	14.3	1.4	14.1	12.3	12.2
	100	9.6	14.3	1.5	13.2	11.4	11.4
	120	8.4	11.5	1.4	13.5	11.0	--
	140	8.6	13.6	1.6	13.3	10.9	--
PiBoA3	25	18.9	28.2	1.5	13.9	16.4	16.2
	60	18.7	25.8	1.4	13.8	16.3	16.5
	120	14.2	19.6	1.4	13.5	13.9	--
	140	14.3	20.9	1.5	13.3	13.8	--
PiBoA4	25	20.2	29.4	1.5	13.9	17.1	17.0
	60	19.9	28.6	1.4	13.8	16.8	17.4
	80	20.2	28.8	1.4	14.1	17.1	17.4
	100	17.5	25.3	1.4	13.2	15.4	15.6
	120	17.1	23.7	1.4	13.5	15.3	--
	140	16.8	25.9	1.5	13.3	15.1	--
PiBoA5	25	31.5	47.9	1.5	13.9	22.7	22.5
	60	30.1	46.6	1.5	13.8	22.0	22.8
	80	31.1	47.3	1.5	14.1	22.6	24.3
	100	29.6	43.0	1.5	13.2	21.4	20.8
	120	25.5	36.5	1.4	13.5	19.5	--
	140	24.3	36.7	1.5	13.3	18.8	--

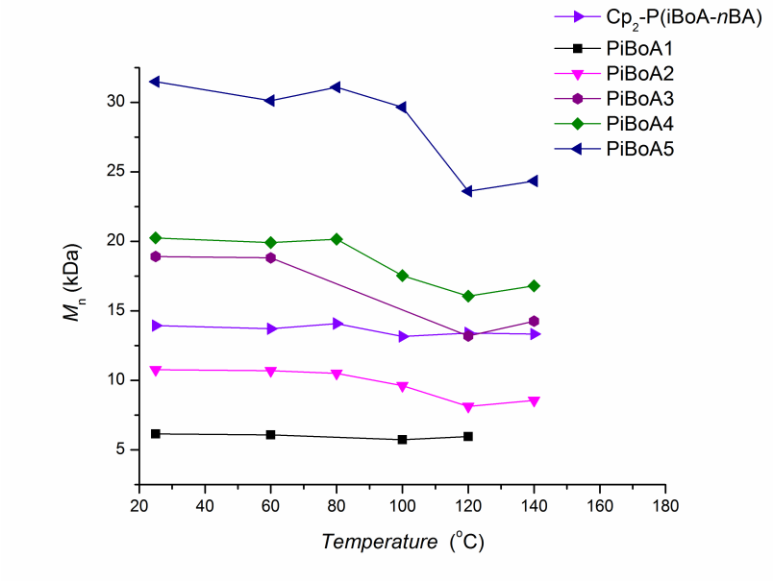


Figure S16. The temperature effect on the M_n values of the PiBoA and Cp_2-P(iBoA-*n*BA) building blocks. All polymers were subjected to elevated temperatures for 24 h; however, the 25°C M_n values correspond to the original untreated polymers.

7.3.3 rDA reactions of the P(Cp-PL) DA polymers

A solution of the DA polymer in toluene (0.4 mM, 250-600 μL) was added to a pressure tube and heated to the desired rDA temperature (*i.e.*, 60, 80, 100, 120, 140°C) for 24 h. After the reaction was rapidly terminated by cooling in liquid nitrogen, ~100 μL was diluted in 1 mL chloroform. The dilute rDA product was dried for 30-45 min under high vacuum to remove the solvent and subsequently characterized immediately by SEC at a concentration of ~2-3 mg mL^{-1}. All temperature controls of the DA polymer building blocks were performed in the same manner as described above for the rDA reactions, except it was not critical that the samples be characterized immediately by SEC.

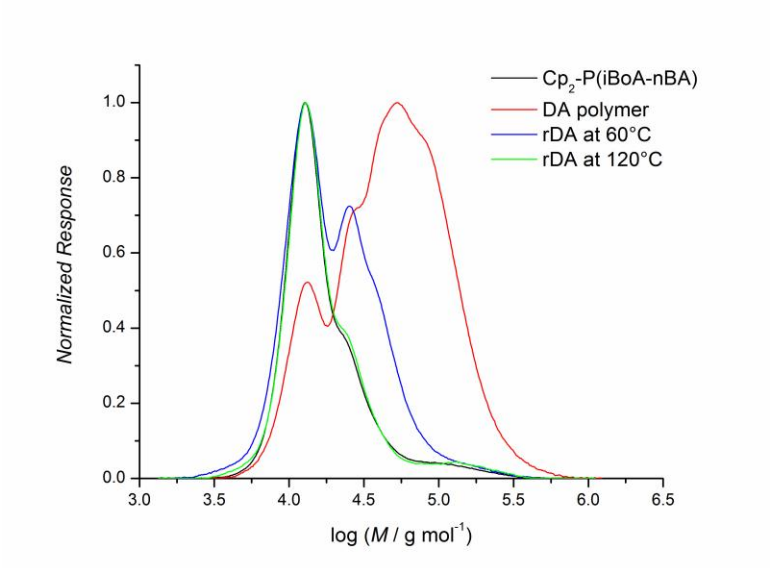


Figure S17. SEC traces of the molecular weight distribution of Cp_2-P(iBoA-*n*BA), the DA polymer P(Cp-PL)1, the DA polymer after 24 h at 60°C, and the DA polymer after 24 h at 120°C.

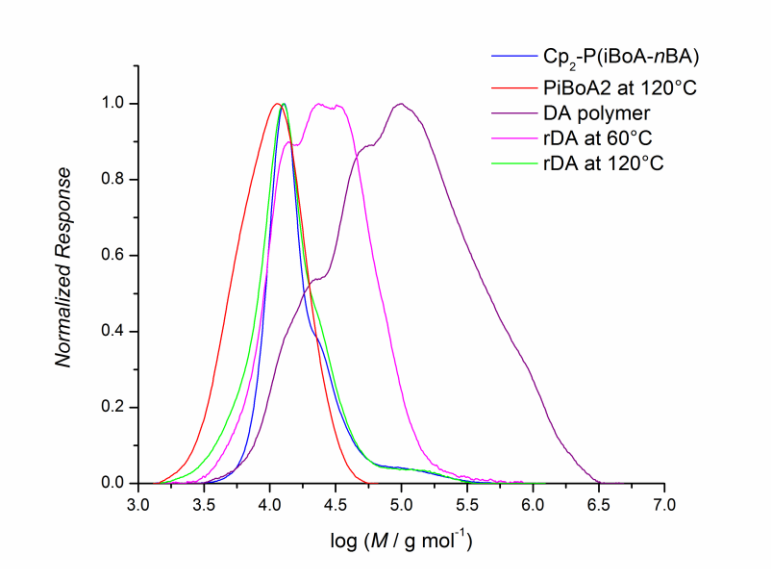


Figure S18. SEC traces of Cp_2-P(iBoA-*n*BA) and PiBoA2 (*i.e.*, DA building blocks), the corresponding DA polymer (P(Cp-PL)3), the molecular weight distribution of the DA polymer after 24 h at 60°C, and the molecular weight distribution of the DA polymer after 24 h at 120°C.

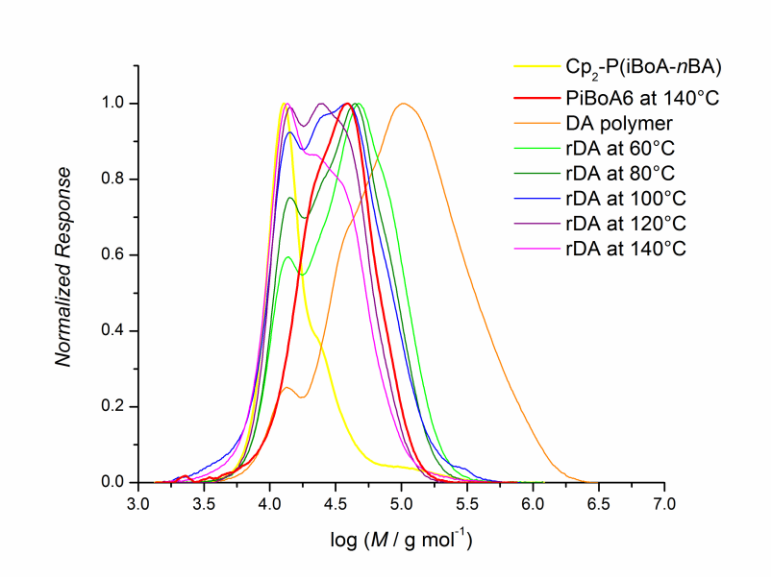


Figure S19. SEC traces of Cp_2-P(iBoA-*n*BA) and PiBoA6 (*i.e.*, DA building blocks), the corresponding DA polymer (P(Cp-PL)7), and the molecular weight distributions of the DA polymer at 60, 80, 100, 120, and 140°C after 24 h.

Table S4. M_n and bonding/debonding values for the Cp_2-P(iBoA-*n*BA)-DA products and their corresponding rDA products. All molecular weight values are determined based on poly(methyl methacrylate) standards and poly(isobornyl acrylate) Mark-Houwink constants.

P-block	DA Bonding (%)	Temp. (°C)	rDA M_n (kDa)	rDA M_w (kDa)	rDA $Đ_M$	rDA Bonding (%)	Decrease in Bonding (%)
P-di-linker	74.9*	60	15.2	24.6	1.6	60.7*	18.9*
		80	15.0	22.3	1.5	58.3	22.2
		100	14.6	23.2	1.6	60.8	18.7
		120	13.9	21.4	1.5	38.7	48.3
		140	12.2	17.2	1.4	-9.1	112.1
PiBoA1	63.7	60	15.2	29.4	1.9	34.5	45.8
		100	10.8	20.5	1.9	12.5	80.4
		120	9.8	17.8	1.8	0.5	99.2
PiBoA2	69.5	60	18.0	32.4	1.8	32.0	53.9
		80	15.0	24.6	1.6	17.8	74.3
		100	12.2	19.7	1.6	7.0	89.9
		120	11.2	18.2	1.6	2.4	96.6
		140	--	--	--	--	--
PiBoA3	57.1	60	21.3	37.0	1.7	24.2	57.6
		120	14.6	20.8	1.4	4.7	91.8
		140	12.5	17.3	1.4	-10.3	118.0
PiBoA4	50.9	60	19.8	32.2	1.6	14.9	70.8
		80	18.7	28.7	1.5	8.6	83.2
		100	16.0	24.9	1.6	4.2	91.7
		120	15.2	20.4	1.3	-0.6	101.1
		140	--	--	--	--	--
PiBoA5	52.5	60	25.4	46.9	1.8	13.5	74.2
		80	23.3	39.8	1.7	3.0	94.4
		100	19.2	36.9	1.9	-11.4	121.7
		120	19.5	29.0	1.5	0.0	100.1
		140	16.9	27.3	1.6	-11.2	121.3

*Different calculation method used, see Section 3.3.1.

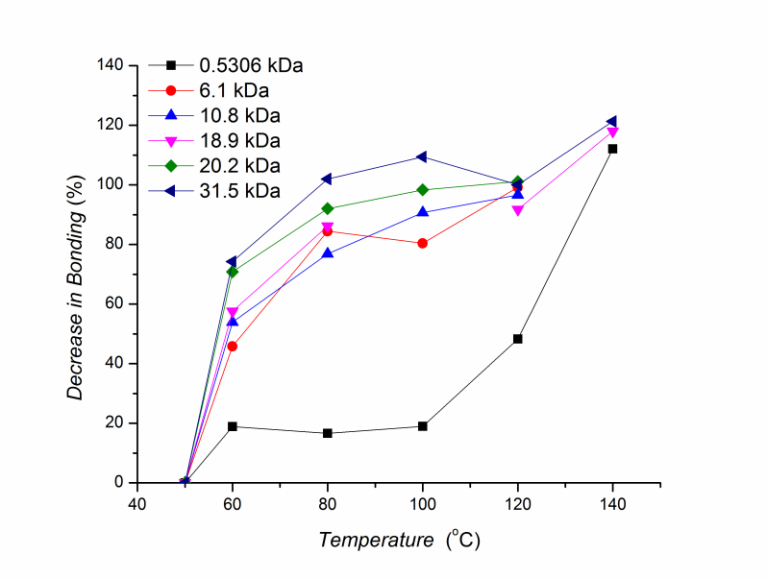


Figure S20. Decrease in bonding achieved for P(Cp-PL) DA products based on different size dienophile di-linkers (indicated in the legend) at temperatures ranging from 60°C to 140°C.

8. *Online* SEC characterization

8.1 SEC (25°C) characterization of the PiBoA and the Cp_2-P(iBoA-*n*BA) building blocks

The building blocks relevant to the *online* HT SEC study (*i.e.*, PiBoA2, PiBoA4, PiBoA5, PiBoA6, and Cp_2-P(iBoA-*n*BA)) were characterized by SEC coupled with a refractive index detector and a static light scattering detector at 25°C prior to analyzing the rDA properties of the DA polymers by the HT SEC system for the *online* temperature dependent measurements. The M_n values determined from refractive index measurements (see Table S5) were utilized to calculate the DP_n values for the evaluation of all the *online* HT SEC rDA reactions. The M_n values determined from light scattering were only employed in referring to the M_n values of the building blocks in figures (*i.e.*, Figure 4b

and Figure 5a in the Manuscript) because the M_n values determined by light scattering are considered to be absolute M_n values.

Table S5. A summary of all polymer building blocks and their respective M_n, M_w, and $Đ_M$ values, determined by refractive index (RI) detection and triple angle static light scattering (SLS) detection in THF at 25°C. Molecular weights were calculated with respect to poly(styrene) standards.

	RI Detection			*SLS Detection*		
Building block	M_n (kDa)	M_w (kDa)	$Đ_M$	M_n (kDa)	M_w (kDa)	$Đ_M$
PiBoA2	5.9	8.8	1.49	9.0	13.5	1.5
PiBoA4	12.0	19.6	1.68	18.9	27.0	1.45
PiBoA5	19.5	35.5	1.82	37.5	59.0	1.57
PiBoA6	31.2	55.5	1.78	59.0	92.7	1.57
Cp_2-P(iBoA-*n*BA)	8.5	16.0	1.88	13.0	16.7	1.29

8.2 SEC (25°C) characterization of DA polymers

All relevant DA polymers were characterized by SEC at 25°C prior to analyzing the rDA properties of these DA polymers by the HT SEC system for the *online* temperature dependent measurements. These M_n values, determined from refractive index measurements, (see Table S6 and S7) were utilized to calculate the DP_{ni} values for the evaluation of all the *online* HT SEC rDA reactions.

8.2.1 P(IS-PL) DA polymers

Table S6. A summary of all P(IS-PL) DA products and their respective M_n, M_w, $Đ_M$ values (measured with the SEC at 25°C), and the calculated bonding percentage. Molecular weights were calculated with respect to poly(styrene) standards.

Polymer	Dienophile	M_n (kDa)	M_w (kDa)	$Đ_M$	Bonding (%)†
P(IS-PL)1	P-di-linker	4.5	15.1	3.36	89*
P(IS-PL)2	PiBoA4	18.7	44.9	2.40	37
P(IS-PL)3	PiBoA5	35.8	134.2	3.75	46
P(IS-PL)4	PiBoA6	86.8	141.2	1.63	64

† $DP_n = M_n / M_{n\text{-PiBoA}}$
* $DP_n = M_n / ((MW_{IPDI\text{-}SA} + MW_{P\text{-di-linker}})/2)$

8.2.2 P(Cp-PL) DA polymers

Table S7. A summary of all relevant P(Cp-PL) DA products and their respective M_n, M_w, $Đ_M$ (measured with the SEC at 25°C), and bonding percentage values. Molecular weights were calculated with respect to poly(styrene) standards. The %Cp_2-P(iBoA-*n*BA) values shown here represent %Cp_2-P(iBoA-*n*BA)$_0$ (see Equation (9)).

Polymer	Dienophile	M_n (kDa)	M_w (kDa)	$Đ_M$	Bonding (%)	%Cp_2-P(iBoA-*n*BA)
P(Cp-PL)1	P-di-linker	20.6	56.6	2.75	78	*
P(Cp-PL)3	PiBoA2	21.2	74.0	3.49	66	*
P(Cp-PL)5	PiBoA4	20.9	56.2	2.69	51	9
P(Cp-PL)6	PiBoA5	29.0	104.0	3.59	51	9
P(Cp-PL)7	PiBoA6	34.4	113.0	3.28	39	13

* The chromatogram of the DA polymer was comprised of molecular weight distributions that were not separated enough to permit deconvolution of the chromatogram and identification of the %Cp_2-P(iBoA-*n*BA) content.

8.3 Building block temperature control study

Table S8. High temperature control M_n, M_w, and $Đ_M$ values for PiBoA as measured by HT SEC in TCB at 80, 90, 100, and 120°C, for the P(IS-PL) DA polymer system. Molecular weights were calculated with respect to poly(styrene) standards.

Building block	Temp. (°C)	M_n (kDa)	M_w (kDa)	$Đ_M$
PiBoA4	80	9.0	16.6	1.84
	90	9.5	18	1.89
	100	9.9	18.2	1.84
	120	13.0	20.1	1.55
PiBoA5	80	14.9	30.2	2.03
	90	19.4	33.4	1.72
	100	16.2	33.2	2.05
	120	18.7	31.4	1.68
PiBoA6	80	24.8	53.7	2.17
	90	28.5	57.0	2.00
	100	27.2	57.2	2.10
	120	34.0	55.0	1.62

Table S9. High temperature control M_n, M_w, and $Đ_M$ values for PiBoA and Cp_2-P(iBoA-*n*BA) as measured by HT SEC in TCB at 80, 100, 110, and 120°C, for the P(Cp-PL) DA polymer system. Molecular weights were calculated with respect to poly(styrene) standards.

Building block	Temp. (°C)	M_n (kDa)	M_w (kDa)	$Đ_M$
PiBoA2	80	5.7	9.2	1.61
PiBoA4	80	12.1	22.9	1.89
	100	12.9	23.9	1.85
	110	13.5	24.8	1.84
	120	14.0	24.9	1.78
PiBoA5	80	20.3	38.5	1.90
	100	20.5	40.6	1.98
	110	24.4	59.7	2.45
	120	25.5	42.6	1.67
PiBoA6	80	40.2	63.5	1.58
	100	39.7	63.1	1.59
	110	45.5	65.2	1.43
	120	44.1	65.3	1.48
Cp_2-P(iBoA-*n*BA)	80	8.1	15.1	1.86
	100	8.6	15.6	1.81
	110	8.8	16.1	1.83
	120	9.3	17.0	1.83

8.4 HT SEC characterization of the rDA properties of the P(IS-PL) DA polymers

Table S10. P(IS-PL) rDA reaction M_n, M_w, and $Đ_M$ values and decrease in debonding % values for HT SEC measurements at 80, 90, 100, and 120°C for near equilibrium reaction times (after 82, 112, 105, and 75 min, respectively. Note, these times include the column run times). The molecular weight of the P-di-linker-based P(IS-PL) was calculated with respect to poly(2-vinylpyridine) standards. Molecular weights of PiBoA-based P(IS-PL)s were calculated with respect to poly(styrene) standards.

Building block	DA Bonding (%)	Temp. (°C)	rDA M_n (kDa)	rDA M_w (kDa)	rDA $Đ_M$	rDA Bonding (%)	Decrease in Bonding (%)
P-di-linker	89	80	-	-	-	-	-
		90	-	-	-	-	-
		100	4.1	7.6	1.8	88.4	1
		120*	3.2	6.1	1.9	83.7	7
PiBoA4	37	80	10.3	250	2.43	12.6	66
		90	11.7	28.1	2.40	18.8	50
		100	11.4	23.0	2.02	13.2	65
		120	12.9	21.0	1.63	-0.8	102
PiBoA5	46	80	18.2	53.8	2.96	18.1	60
		90	24.4	48.1	1.97	20.5	55
		100	17.4	43.8	2.52	6.9	85
		120	18.9	33.6	1.78	1.1	98
PiBoA6	64	80	34.2	87.4	2.56	27.5	57
		90	32.9	79.0	2.4	13.3	79
		100	26.5	73.0	2.75	-2.6	104
		120	35.0	55.0	1.57	2.9	96

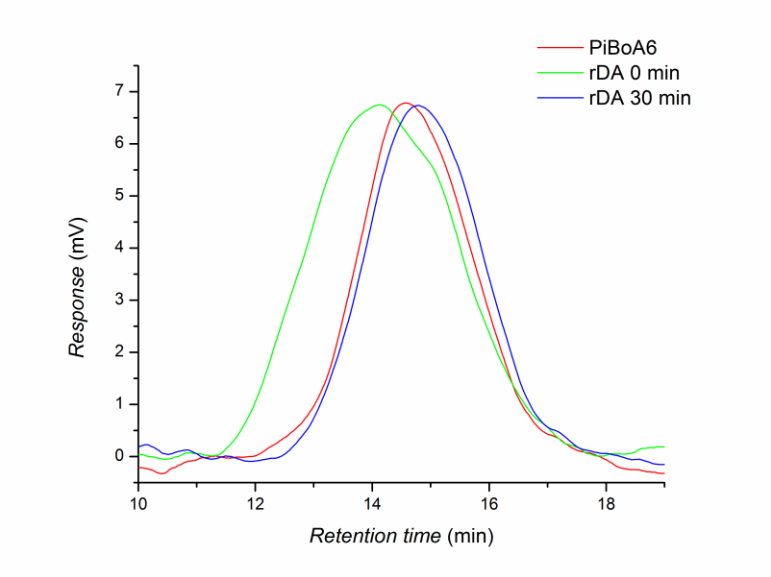


Figure S21. *Online* HT SEC characterization of the rDA reaction of the P(IS-PL)4 (*i.e.*, IPDI-SA+PiBoA6) DA polymer. Chromatograms for the 0 min and 30 min heating times at 120°C are shown. Note, that these heating times correspond to ~ 15 min and 45 min reaction time because of the extra ~15 min residence time in the column (which is also at 120°C).

8.5 HT SEC characterization of the rDA properties of the P(Cp-PL) DA polymers

Table S11. P(Cp-PL) DA polymer rDA reaction M_n, M_w, and $Đ_M$ values and decrease in debonding % values for HT SEC measurements after 300 min. Molecular weights were calculated with respect to poly(styrene) standards.

Building block	DA Bonding (%)	Temp. (°C)	rDA M_n (kDa)	rDA M_w (kDa)	rDA $Đ_M$	rDA Decrease in Bonding (%)	Normalized Cp_2 content (%)**
P-di-linker	78	80	7.2	14.7	2.0	41	N/A
		100	7.7	14.2	1.8	48	N/A
		110	8.2	14.5	1.8	45	N/A
		120	8.0	15.2	1.9	50	N/A
PiBoA2	66	80	7.4	12.4	1.7	15	N/A
		100	-	-	-	-	-
		110	-	-	-	-	-
		120*	5.5	11.7	2.1	66	N/A
PiBoA4	51	80	9.9	19.3	2.1	97	64.3
		100	9.5	18.7	1.9	126	68.9
		110	9.7	18.5	2.0	127	83.9
		120*	9.7	18.5	1.9	139	65.2*
PiBoA5	51	80	12.2	29.8	2.4	128	65.2
		100	12.8	28.5	2.2	131	76.0
		110	11.7	26.9	2.3	127	87.4
		120*	12.2	26.2	2.1	184	46.6*
PiBoA6	39	80	17.8	47.7	2.7	185	81.5
		100	16.4	44.9	2.7	221	85.4
		110	15.4	44.4	2.9	296	96.4
		120*	16.9	44.0	2.6	249	33.7*

N/A The chromatogram of the DA polymer was comprised of molecular weight distributions that were not separated enough to permit deconvolution of the chromatogram and identification of the $\%Cp_2$-P(iBoA-*n*BA).

* Assumed to represent the 100% debonding point $\%Cp_2\text{-P(iBoA-}n\text{BA)}_{max}$.

** See Section 8.2.2 for $\%Cp_2\text{-P(iBoA-}n\text{BA)}_0$ values and Section 3.4.2 for Equation (9).

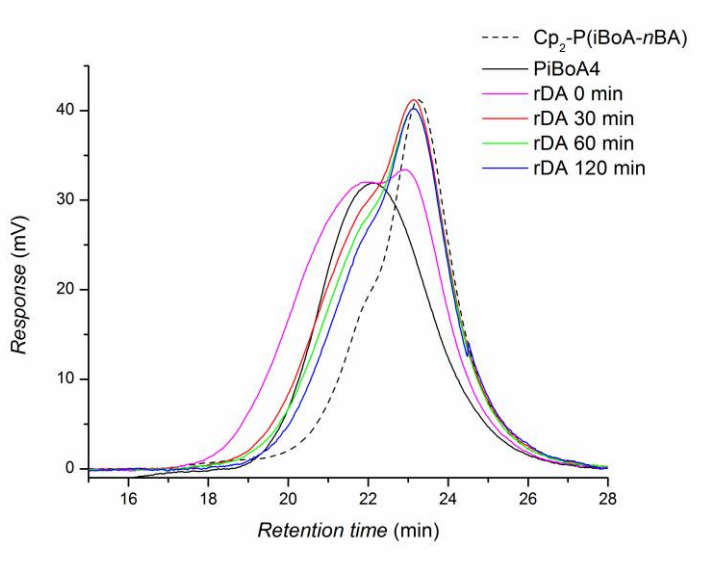


Figure S22. *Online* HT SEC characterization of the rDA reaction of the P(Cp-PL)5 (*i.e.*, Cp_2-P(iBoA-*n*BA)+PiBoA4) DA polymer. Chromatograms for the 0, 60, 30, and 120 min heating times at 80°C are shown. Note, that these heating times correspond to ~22 min, ~52 min, ~82 min, and ~142 min of reaction time because of the extra ~22 min residence time in the column (which is also at 80°C temperature).

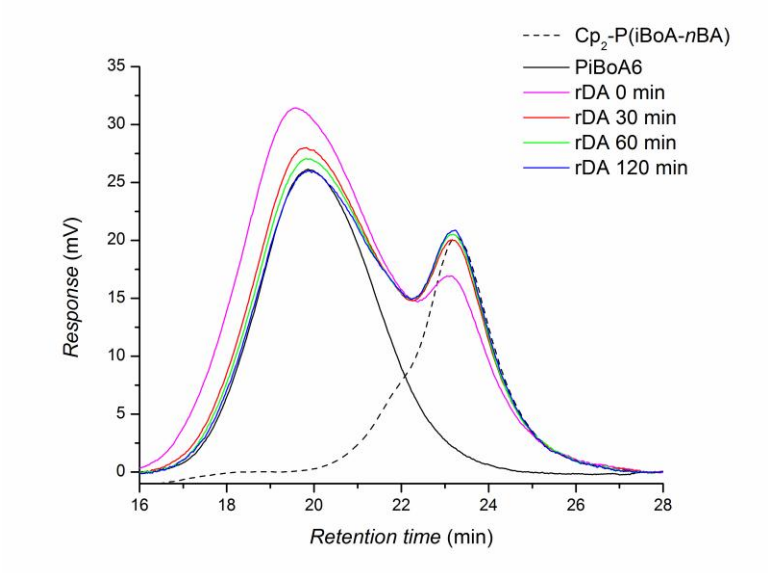


Figure S23. *Online* HT SEC characterization of the rDA reaction of the P(Cp-PL)7 (*i.e.*, Cp_2-P(iBoA-*n*BA)+PiBoA6) DA polymer. Chromatograms for the 0, 30, 60, and 120 min at 80°C are shown. Note, that these heating times correspond to ~20 min, ~50 min, ~80 min, and ~140 min of reaction time because of the extra ~20 min residence time in the column (which is also at 80°C temperature).

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