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Formation of active centers of polymer catalysts for radical-coordination polymerization

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Initial reagents: monomers (MMA made by MMA LLC, Dzerzhinsk, Russia, styrene by Fluka, AllCl by Fluka), initiators (AIBN and Bz_2O_2) and solvents (toluene, methanol, chloroform, tetrahydrofuran, acetonitrile) after purification under generally accepted methods corresponded to the literature data in their characteristics; Cp_2Fe by Sigma-Aldrich, USA (CAS Number 102-54-5).

Methods of the experiment:

1) A weight of 0.3086 g of Cp_2Fe/AIBN mixture taken in a molar ratio of 1:2 was dissolved in 6 mL of toluene. The solution was placed in an ampoule with a rubber membrane and a screw cap and purged through a needle with argon to remove air. The ampoule was kept in a thermostat at 90°C for 9 h (the time corresponds to the flow rate of $[AIBN]_0$ = 0.2 mol/L to $[AIBN]_t = 10^{-8}$ mol/L). The resulting product was analyzed by mass spectrometry.
2) A weight of 0.0423 g of Cp_2Fe/Bz_2O_2 mixture taken in a molar ratio of 1:10 was dissolved in 2 mL of toluene. The solution was placed in a glass ampoule and degassed by threefold repetition of freezing-vacuuming-thawing cycles, thereafter the ampoule was sealed and kept in a thermostat at 100°C for 15 h (corresponding to the consumption of $[Bz_2O_2]_0$ = 0.01 mol/L to $[Bz_2O_2] = 10^{-6}$ mol/L). The resulting product was analyzed by mass spectrometry.
3) A weight of 0.3086 g of Cp_2Fe/AIBN mixture taken in a molar ratio of 1:2 was dissolved in a mixture of 5.4 mL of toluene and 0.6 mL of monomer. The solution was placed in an ampoule and kept in a thermostat at 100°C for 3 h (the time corresponds to the flow rate of $[AIBN]_0$ = 0.2 mol/L to $[AIBN]_t = 10^{-8}$ mol/L). The resulting product was analyzed by mass spectrometry.

4) Electrospray ionization mass spectra (ESI) were obtained on a LCMS-2010 EV (Shimadzu) liquid quadrupole chromatography-mass spectrometer (syringe sample injection, eluent – acetonitrile, flow rate 0.1 mL/min) in the mode of positive and negative ions registration at capillary potential 4.5 and -3.5 kV. The heater temperature was 200°C and the evaporator temperature was 230°C, with flow rate of nebulizing (atomizing) gas (nitrogen) being 1.5 L/min (Cp_2Fe/AIBN; Cp_2Fe/AIBN/monomer). In the infusion analysis mode (Cp_2Fe/Bz_2O_2) continuous injection of the sample in a solution of toluene and acetonitrile (70/30 ratio) at 0.01 mL/min was made. When analyzing ions in mass spectra, peaks with intensities of at least 600 were used. The m/z values were rounded to whole numbers.
5) Quantum chemical calculations were made with Priroda 17 program using the Perdue-Burke-Ernzerhoff density functional [D. N. Laikov and Y. A. Ustynyuk, *Russ. Chem. Bull.*, 2005, **54**, 820] and the triple-split basis (PBE/3z). The chosen method is optimal for calculating both geometric and energetic parameters of the analyzed molecules. The radicals of the corresponding monomers with an attached methyl group acting as the chain-end were used as models for the growth radicals of styrene, MMA, and AllCl (vinyl type), with the advantage of this structure over larger radicals being proved in [A. V. Smirnov, E. A. Valiakhmetov, D. R. Diniakhmetova and S. V. Kolesov, *Butlerov Commun., A*, 2023, **74**, 5, 24]. The geometry of the structures analyzed was optimized without symmetry constraint. Absolute enthalpies were calculated by formula: $H^{\circ}_{298} = E_{tot} + \varepsilon_{ZPV} + H_{corr}$, where E_{tot} is total energy, ε_{ZPV} – zero- point energy, H_{corr} – thermal correction. The change in enthalpy of reaction (ΔH°) and enthalpy of activation ($\Delta H^{\neq}$) was found by calculating the difference between the absolute enthalpies H° of reaction products and reactants. All energetic parameters were calculated at 298 K. The type of stationary point on the potential energy surface of the system under study (minimum, saddle point) was identified by calculating the matrix of force constants (Hessian matrix). The spin density was calculated by the Hirschfeld method.
6) The molecular characteristics (M_w, M_n and D) of poly(methyl methacrylate) (PMMA) were determined by gel permeation chromatography on a MAESTRO HPLC liquid chromatograph (eluent: tetrahydrofuran, flow rate: 1.0 mL/min). The Mark-Kuhn-Hauwink equation constants ($K = 8.97\times10^{-5}$; $\alpha = 0.71$ at $T = 30$ °C in tetrahydrofuran) were used to calculate the molecular weights.
7) The microtacticity of PMMA was determined by ^{1}H NMR spectroscopy at 25ºC using Brucker AV-500 device for the polymer solution in $CDCl_3$ by the signals of α-methyl groups: syndiotacticity at ($\delta = 0.8$-0.9 ppm), heterotacticity at ($\delta = 0.95$-1.0 ppm), isotacticity at ($\delta = 1.05$-1.1 ppm).

Table S2. Results of chromatography-mass spectrometry analysis of products of thermalyzed mixture of Cp_2Fe/AIBN/styrene in toluene

Product [a]	*n* [b]	*m/z, calc.*	*m/z, exp.*	*I*	Associate		
					m/z, calc.	*m/z, exp.*	*I*
4	2	367	367	2485	408	408	30285
	3	471	471	3407	512	512	13459

Notes hereinafter: [a] – designations correspond to products of reactions of oligomer formation; [b] – degree of polymerization in the oligomer formulas.

Table S3. Results of chromatography-mass spectrometry analysis of thermalized Cp_2Fe/AIBN/MMA mixture products in toluene

Product [a]	*n* [b]	*m/z, calc.*	*m/z, exp.*	*I*	Associate		
					m/z, calc.	*m/z, exp.*	*I*
4	4	559	559	3231	600	600	682
5	6	759	759	3347	–	–	–
	6	–	–	–	808	808	603

Table S4. Energy characteristics (kJ/mol) of the interaction between $(CH_3)_2C^{\bullet}CN$ and a number of monomers and FC

Energetic characteristics	Molecule			
	AllCl	MMA	styrene	Cp_2Fe
Enthalpy of reaction, ΔH^0	-35.1	-54.9	-61.4	4.1
Enthalpy of activation, $\Delta H^{\#}$	28.3	22.1	18.8	45.5

Table S5. Spin characteristics of a number of free radicals

Radical	Spin density, a.u.	Radical	Spin density, a.u.
2-cyanoprop-2-yl	0.48	styryl	0.45
benzyloxy-	0.47 0.47	methyl methacrylate	0.51
benzyl	0.50	allyl chloride	0.59
phenyl	0.76	ferrocenyl	0.99

Table S6. Molecular characteristics of PMMA homopolymers obtained by different methods of polymerization initiation, at T = 60 °C

System	$M_w \times 10^5$	$M_n \times 10^5$	D	Triads, %		
				s-	*h*-	*i*-
Cp_2Fe/AIBN/AllCl	7.9	3.9	2.0	64.6	32.7	2.7
AIBN	31.4	14.0	2.2	55.0	43.0	2.0

Table S7. The structures of monomers and initiators

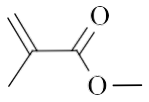
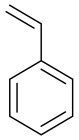
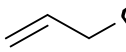
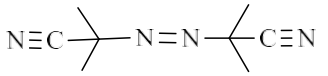
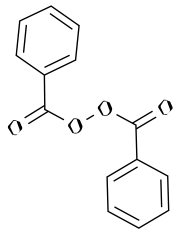
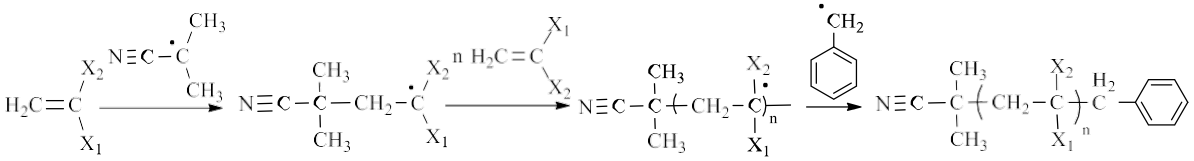
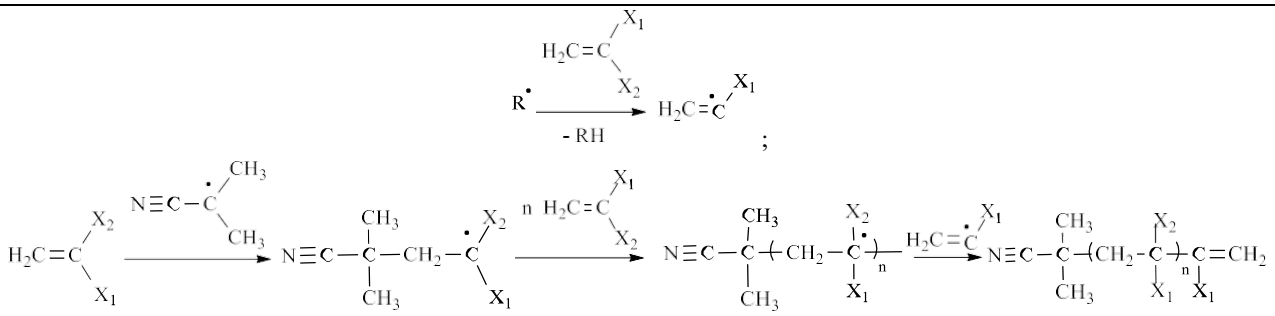
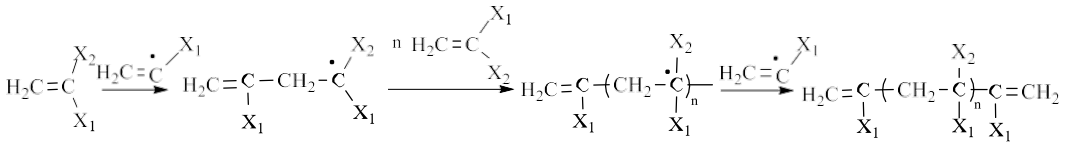
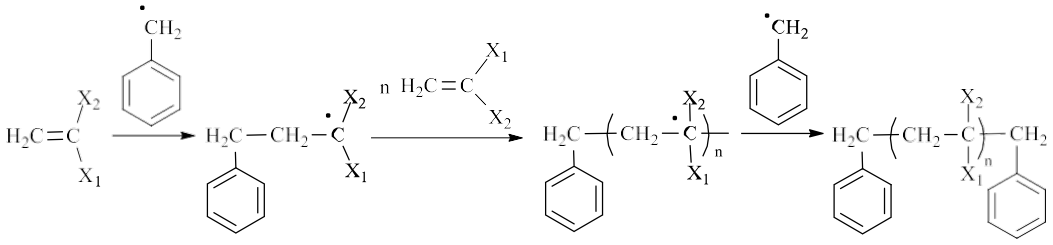
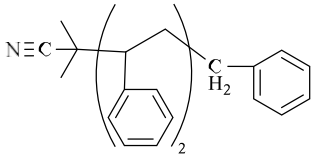
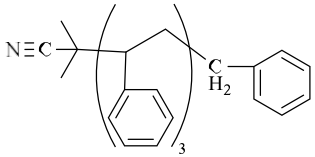
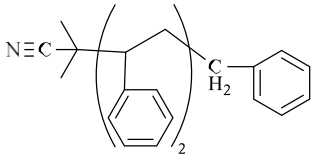
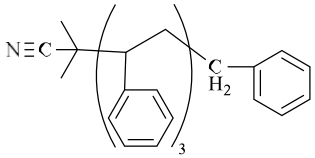
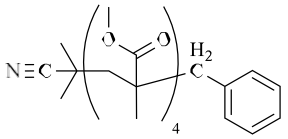
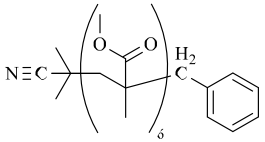
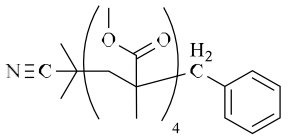
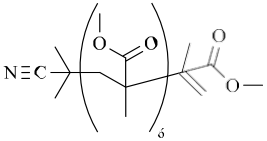
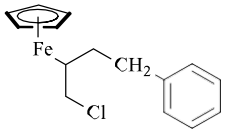
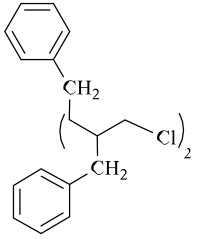
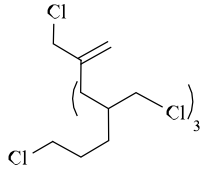
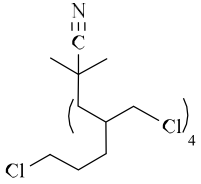
	MMA
	styrene
	AllCl
	AIBN
	Bz_2O_2

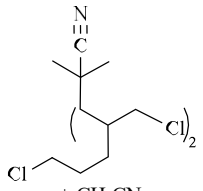
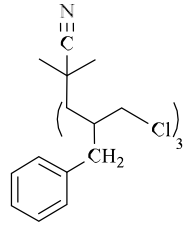
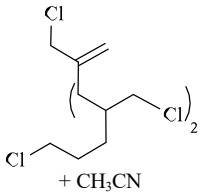
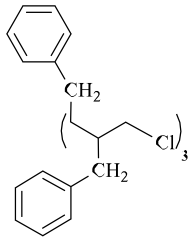
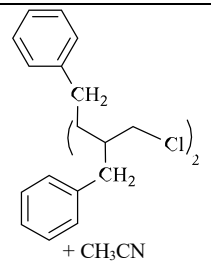
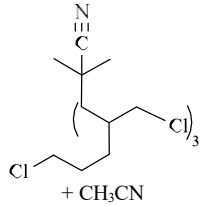
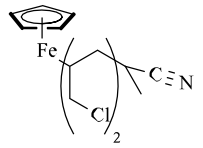
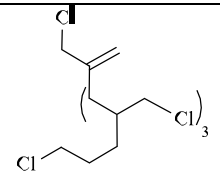
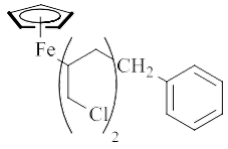
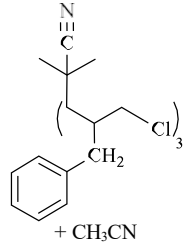
Table S8. Reactions forming end functional groups

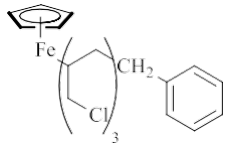
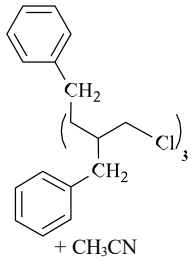
4	
5	
6	
7	

$X_1 = COOCH_3$; C_6H_5; CH_2Cl,
$X_2 = CH_3$ (poly(methyl methacrylate)); H (polystyrene, poly(allyl chloride))

Table S9. The most relevant species that were observed in the spectra

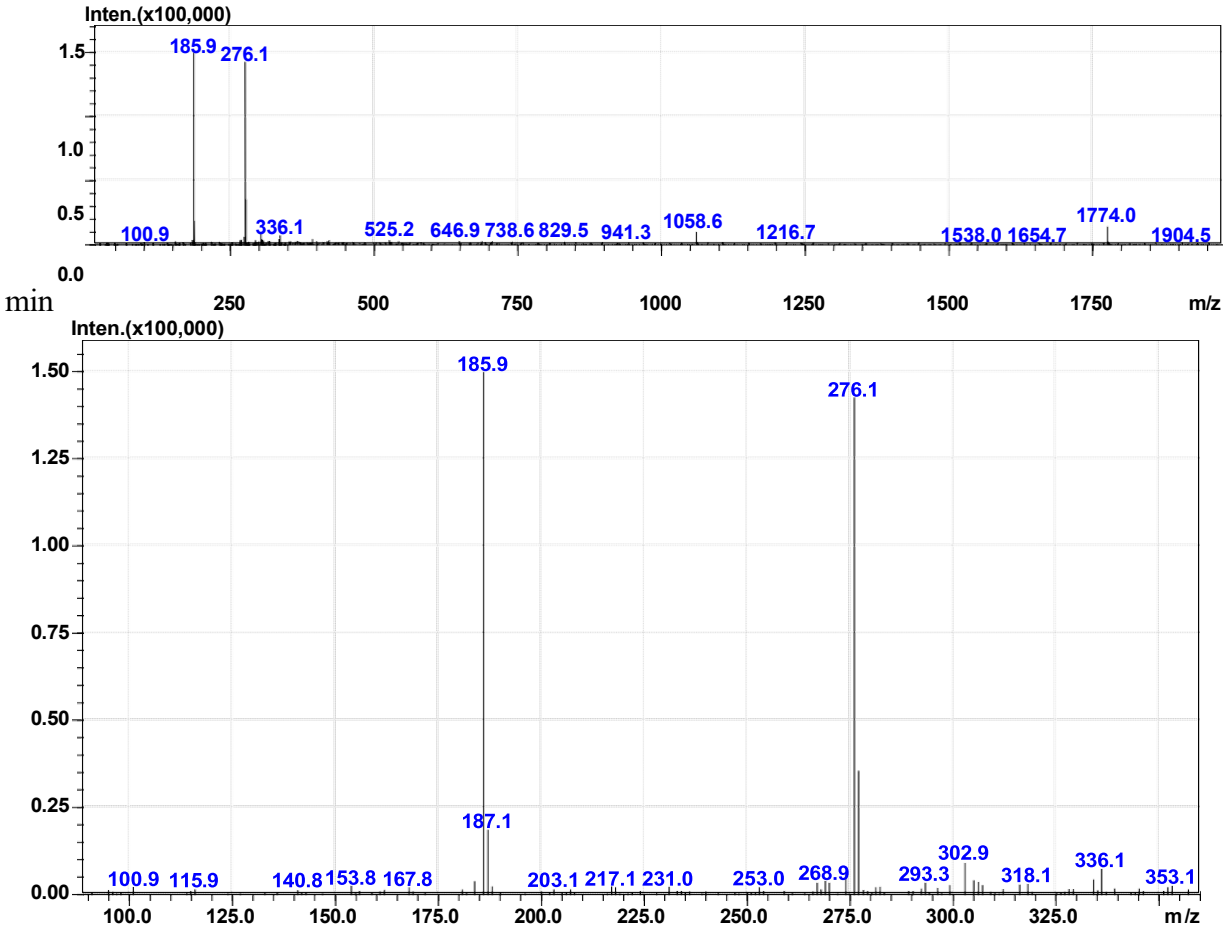
monomer	oligomer n = 1		n = 2		n = 3		n = 4		n = 5		n = 6	
	m/z, calc.	structure	m/z, calc.	structure	m/z, calc.	structure	m/z, calc.	structure	m/z, calc.	structure	m/z, calc.	structure
styrene	–	–	367		471		–	–	–	–	–	–
			408	 + CH_3CN	512	 + CH_3CN	–	–	–	–	–	–
MMA	–	–	–	–	–	–	559		–	–	759	
							600	 + CH_3CN			808	 + CH_3CN
AllCl	329	 + CH_3CN	334		380		449		–	–	–	–

			338		387							
			345		410							
			375		414							
			382		421							
			405		428							

					440							
					451	 + CH_3CN						

Mass spectrum of positive ESI ions of thermal transformation products in Cp_2Fe and AIBN mixture in toluene

MeCN 0.1 ml/min
Scan (C+) Ret. Time : 2.600 - 0.150



Mass spectrum of positive ESI ions of thermal transformation products in Cp_2Fe, AIBN and styrene mixture in toluene

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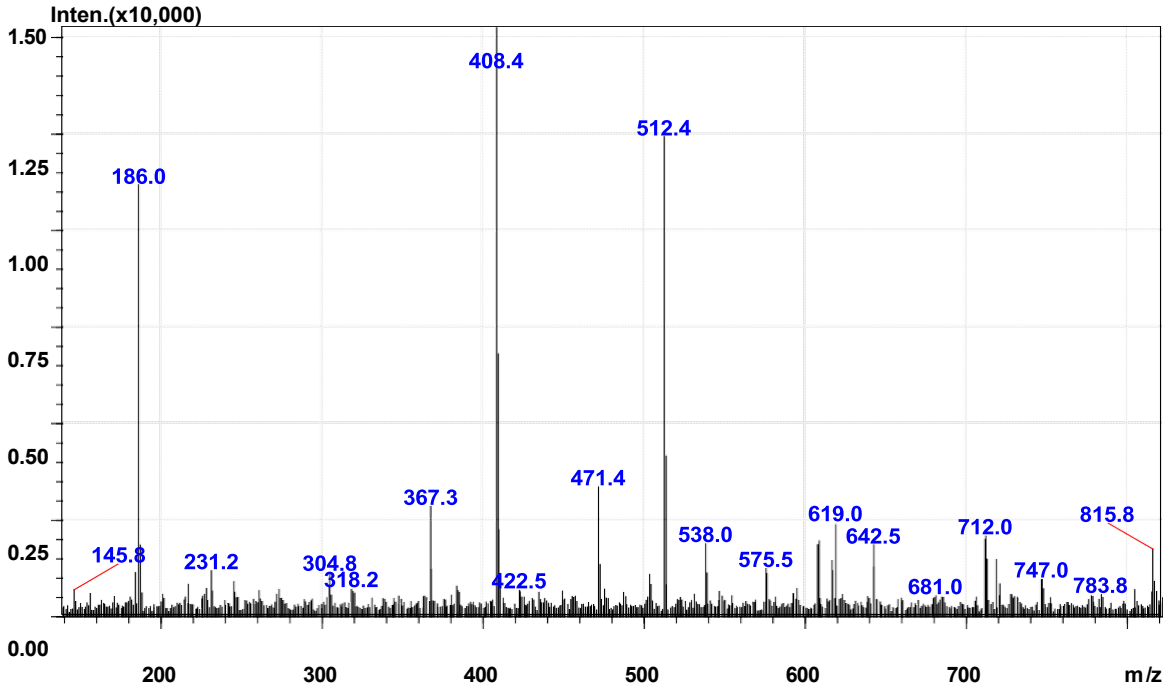

Mass spectrum of positive ESI ions of thermal transformation products in Cp_2Fe, AIBN and MMA mixture in toluene

MeCN 0.1 ml/min
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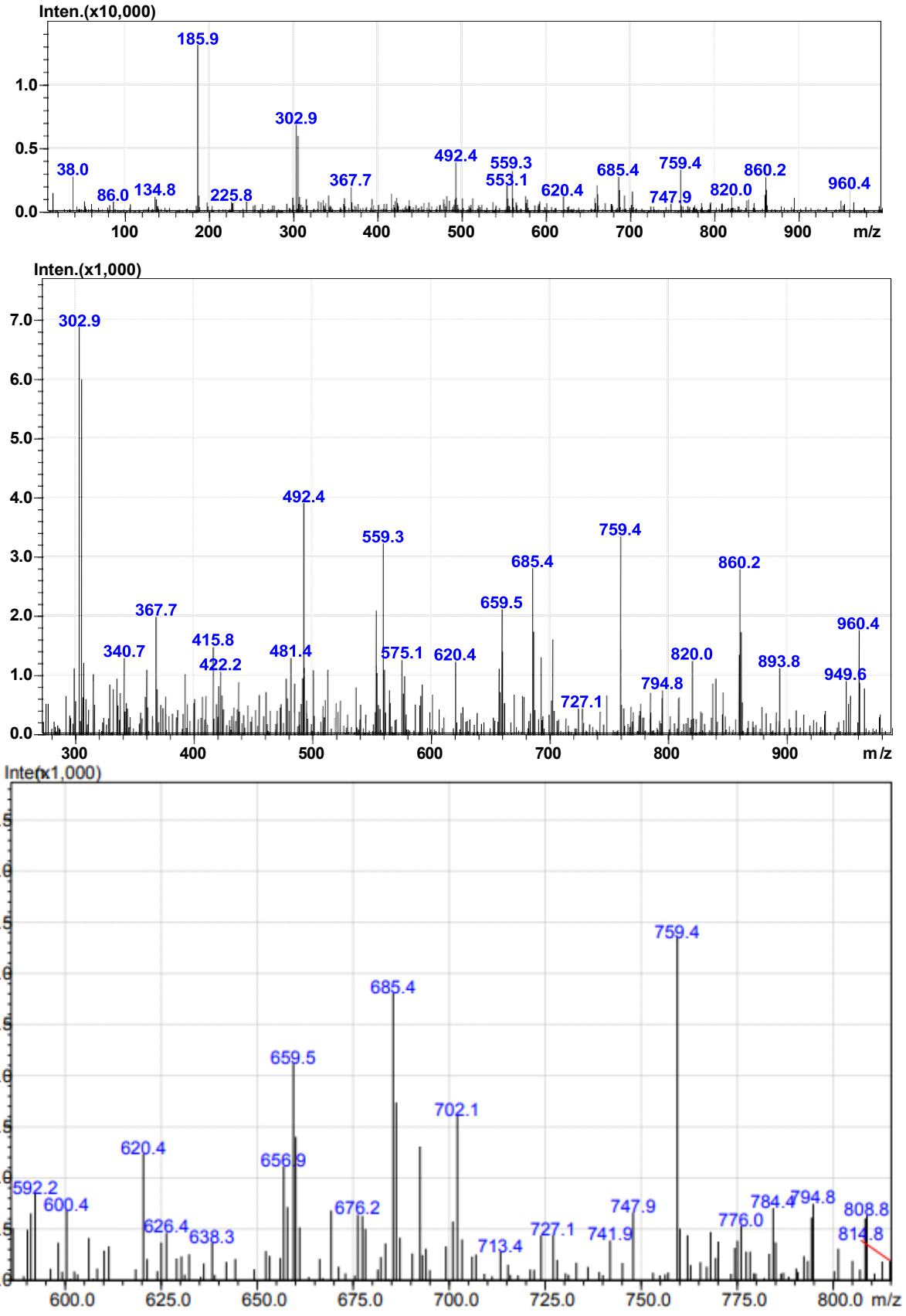
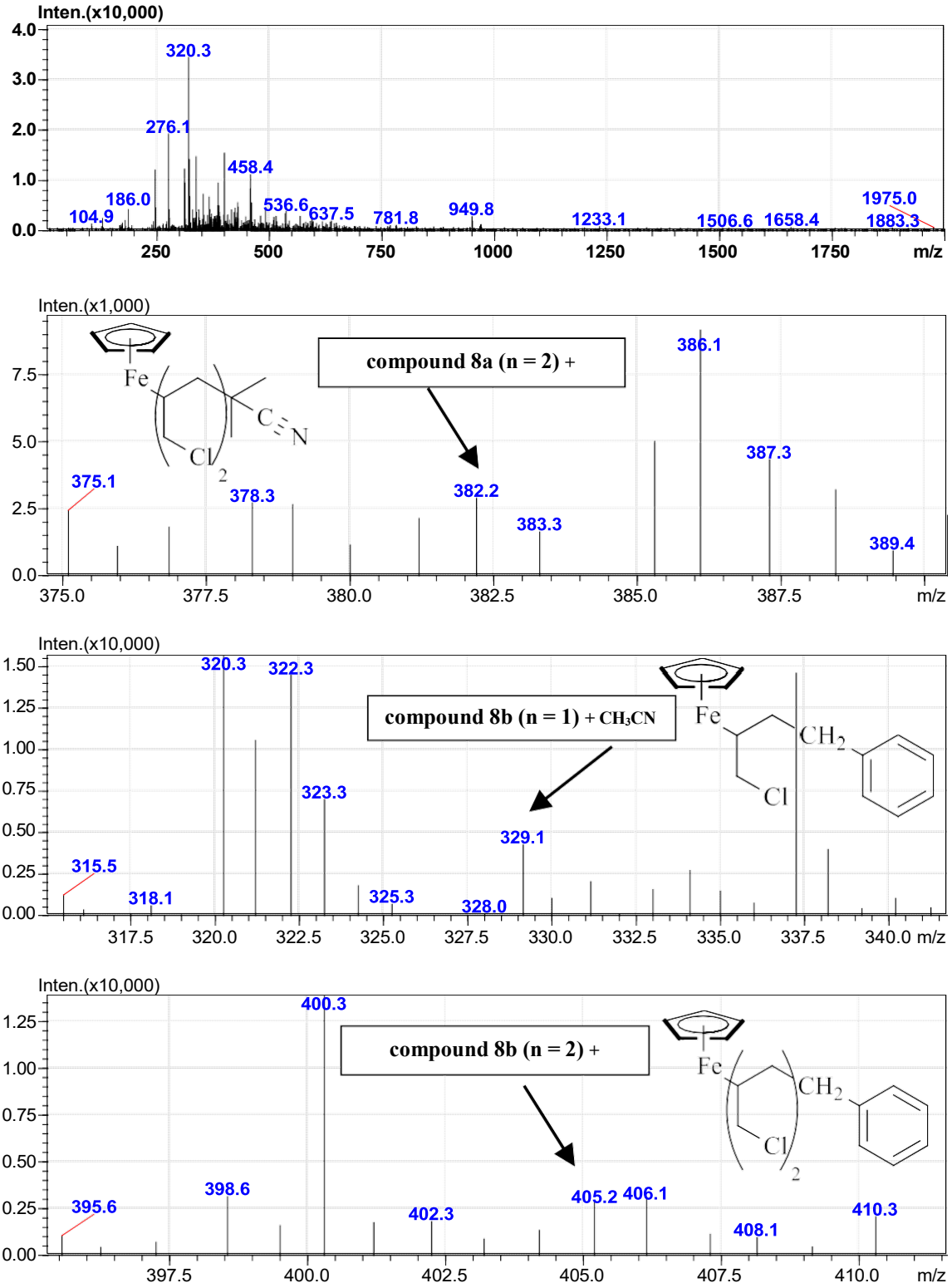


Mass spectrum of positive ESI ions of thermal transformation products in Cp_2Fe, AIBN and AllCl mixture in toluene

MeCN 0.1 ml/min
Scan(C+) Ret. Time : 1.600 -> 1.700 min



Quantum-chemical calculations

Initial reagents:

$(CH_3)_2C^{\bullet}CN$ (2-cyanoprop-2-yl radical)

E_{total} = -210.53696378297
Cartesian:

6	0.218060910	-0.037759040	-0.208987980
6	-0.553413900	1.244554290	-0.150722050
1	-0.442367240	1.718304550	0.839761270
1	-0.228717330	1.957507210	-0.916189970
1	-1.632127660	1.053633300	-0.283967950
6	-0.088268990	-1.133936380	0.764382430
1	0.045515040	-0.779620170	1.800907050
1	-1.143299030	-1.445543780	0.676919810
1	0.548100470	-2.012214160	0.611633970
6	1.215327850	-0.209590810	-1.162504100
7	2.061189880	-0.355335010	-1.971232470

AllCl (monomer – allyl chloride)

E_{total} = -577.22021786629
Cartesian:

1	1.098040640	0.460867830	-1.508962330
6	1.319114140	-0.031954290	-0.560383570
1	2.341750130	-0.374721700	-0.406545760
6	0.376626410	-0.204975770	0.372062280
1	0.612167470	-0.711201900	1.311540180
6	-1.022986020	0.277386760	0.219043170
1	-1.185842340	0.785122960	-0.737291880
17	-2.205115110	-1.126599050	0.264117830
1	-1.333755310	0.926075160	1.046420080

$CH_3CH_2C^{\bullet}HCH_2Cl$ (modeling poly(allyl chloride) growth radical)

E_{total} = -617.06238390915
Cartesian:

6	-0.122346180	0.569780710	-0.472008620
1	-1.094126690	1.069493250	-0.494990450
6	0.026773700	-0.637920030	0.385153540
1	-0.314173080	-1.523411650	-0.190462750
1	1.095674880	-0.821829820	0.586967090
6	0.857220740	0.944403460	-1.476344520
1	0.780560240	1.978419230	-1.821078110
1	1.887815100	0.679223370	-1.221249520
17	0.563603030	-0.052316550	-3.089976780
6	-0.766341110	-0.564943110	1.696980210
1	-0.419300060	0.267816510	2.324166830
1	-1.837431110	-0.415222470	1.499489820
1	-0.657929450	-1.493492910	2.273353260

Cp_2Fe (ferrocene)

E_{total} = -1650.3021719709
Cartesian:

26	0.000036560	-0.000240350	0.000091840
6	-1.647844070	1.137234880	-0.442221850
6	-1.647637160	0.772675580	0.944950940
6	-1.648203650	-0.659256870	1.026882000
6	-1.648673790	-1.179673430	-0.309629520
6	-1.648413930	-0.069387500	-1.217602670
1	-1.626662830	2.149135030	-0.836262740
1	-1.626310170	1.460122440	1.785556080
1	-1.627579910	-1.246303880	1.940450570
1	-1.628473060	-2.229928860	-0.585695970
1	-1.627775420	-0.131410980	-2.301753190
6	1.648114150	1.136182130	-0.444288700
6	1.647796660	-0.071199750	-1.218483810
6	1.648089670	-1.180599980	-0.309429180
6	1.648615230	-0.658866790	1.026571270
6	1.648556530	0.772989170	0.943239620
1	1.626877590	2.147689300	-0.839332150
1	1.626200770	-0.134270370	-2.302554600
1	1.627315040	-2.231122150	-0.584432330
1	1.628211090	-1.244993940	1.940734870
1	1.627760710	1.461226320	1.783209540

Interactions of a $(CH_3)_2C^{\bullet}CN$ radical with AllCl:

$Me_2C(CN)CH_2C^{\bullet}H\,CH_2Cl$

E_{total} = -787.77419562255
Cartesian:

6	-0.858858420	0.613114280	-0.091271340
6	-1.283341800	-0.178024700	1.163856310
1	-0.935974220	-1.216281750	1.080679210
1	-0.846060920	0.256356700	2.071798460
1	-2.375933000	-0.175870460	1.268796610
6	-1.519765870	0.025272140	-1.357410350
1	-1.255367010	-1.034940950	-1.463528180
1	-2.612374000	0.095086200	-1.283420040
1	-1.201415880	0.563675400	-2.260024120
6	-1.308273940	2.007986980	0.056633130
7	-1.652931700	3.113646750	0.172488280
6	1.377652770	-0.649216590	-0.428969250
1	0.980774450	-1.343994710	-1.170510400
6	0.704903700	0.662682960	-0.224987720
1	1.117114820	1.163983670	0.663612370
1	0.928205770	1.323541430	-1.085400450
6	2.521818590	-1.080646730	0.359820630
1	3.186968150	-1.775180370	-0.159876590
1	3.081023490	-0.262400250	0.823228040
17	1.951835030	-2.108789990	1.864485420

TS

E_{total} = -787.74763832783

Cartesian:

6	-1.116468990	0.624221150	-0.015297070
6	-1.198812510	0.028549830	1.369277910
1	-0.695016860	-0.946833650	1.399050110
1	-0.762526420	0.690345980	2.127826970
1	-2.256099550	-0.134751500	1.641856380
6	-1.563367660	-0.243532690	-1.166063540
1	-1.068597660	-1.222486920	-1.117232720
1	-2.652269780	-0.412844310	-1.107317990
1	-1.351150040	0.221023500	-2.137013230
6	-1.418971660	2.006368130	-0.116258740
7	-1.615451900	3.158359780	-0.206733090
6	1.680385380	-0.358606130	-0.630669680
1	1.699038800	-0.741940350	-1.653294420
6	1.079992380	0.850506320	-0.365948240
1	1.208514300	1.315098760	0.613127990
1	0.883371480	1.534789030	-1.190389460
6	2.275347080	-1.223148770	0.405722440
1	3.276210910	-1.579990830	0.138344730
1	2.288314860	-0.759674150	1.397326520
17	1.307557830	-2.805453160	0.613685130

Interactions of a $(CH_3)_2C^{\bullet}CN$ radical with Cp_2Fe:

Cp-Fe-(C_5H_5R)

E_{total} = -1860.8411514227

Cartesian:

26	-1.489592620	-0.309610170	0.272131480
6	-3.136852680	0.096840810	-1.021471480
6	-3.262423340	0.833557310	0.193612180
6	-3.343698460	-0.106687140	1.276795370
6	-3.234387920	-1.417873140	0.728104210
6	-3.086144290	-1.290758420	-0.695572210
1	-3.028021710	0.521419080	-2.016032060
1	-3.307612640	1.914898750	0.283584870
1	-3.457246260	0.142254650	2.327728390
1	-3.249269860	-2.350242320	1.284652770
1	-2.971409380	-2.108920170	-1.400302410
6	0.765270260	0.216512460	-0.568297690
6	0.263344870	-1.192475000	-0.275214070
6	0.024716770	-1.333065650	1.127584980
6	-0.080216520	-0.014723170	1.683085830
6	0.099864350	0.918263050	0.612318130
1	0.365411740	0.586395420	-1.528316180
1	0.387603120	-2.024209630	-0.965298950
1	-0.117501590	-2.265703310	1.668065870
1	-0.313023050	0.225293590	2.717714490
1	0.058819860	1.998813740	0.732248860
6	2.350952560	0.400872290	-0.703505170
6	2.664496620	1.879477250	-1.014160710

1	3.739727280	2.022100230	-1.184216820
1	2.126276790	2.219921260	-1.908836230
1	2.363895950	2.504877410	-0.162608960
6	3.113864220	-0.061665140	0.551361140
1	4.194808310	0.065816560	0.405353140
1	2.804514450	0.541930120	1.414684020
1	2.916684330	-1.116980620	0.774125370
6	2.767376100	-0.419816670	-1.847995350
7	3.069772730	-1.076513420	-2.761322810

TS

E_{total} = -1860.8230482772

Cartesian:

26	-1.524032170	-0.331356380	0.324844280
6	-3.026691180	0.097969240	-1.063218930
6	-3.223361410	0.846460300	0.139598550
6	-3.378386950	-0.083815040	1.221773930
6	-3.259287250	-1.404967770	0.686742750
6	-3.031645040	-1.291651020	-0.726487040
1	-2.853904040	0.512918170	-2.052426180
1	-3.248541730	1.929129280	0.220753730
1	-3.538657190	0.171631030	2.265058020
1	-3.312200310	-2.330842720	1.251835750
1	-2.882085350	-2.116177950	-1.417137740
6	0.477517460	0.162723440	-0.481340370
6	0.225554260	-1.243190630	-0.167670760
6	-0.021558310	-1.359904750	1.237818290
6	-0.133078300	-0.038025400	1.781174050
6	0.052373130	0.896786760	0.709893210
1	0.300139380	0.555267320	-1.482297870
1	0.357012580	-2.064714150	-0.865645590
1	-0.147284780	-2.287612940	1.789137710
1	-0.355096490	0.210118010	2.815379050
1	0.005324840	1.978364630	0.798822000
6	2.596782940	0.438622810	-0.782452730
6	2.700475540	1.926109600	-1.039014140
1	3.749741900	2.220199440	-1.212736900
1	2.122173980	2.232106000	-1.920850610
1	2.341685700	2.489027010	-0.165500620
6	3.239638240	-0.068977500	0.485851110
1	4.332170730	0.084657520	0.454864370
1	2.850156750	0.479980460	1.354965360
1	3.055007810	-1.139673570	0.635630840
6	2.743699850	-0.388336230	-1.926752670
7	2.786355420	-1.082824970	-2.870610850

Interactions of a $CH_3CH_2C^{\bullet}HCHCl$ radical with Cp_2Fe:

Cp-Fe-(C_5H_5R)

E_{total} = -2267.3789450389

Cartesian:

6	-1.800948500	-0.449932460	-1.336564650

1	-2.751113840	-0.512592470	-0.777714570
6	-1.600993450	-1.763477100	-2.112951530
1	-2.328402570	-1.782582590	-2.938566540
1	-0.603350990	-1.753575920	-2.583906320
6	-1.891000430	0.751219090	-2.269316920
1	-1.948710800	1.695164880	-1.720487180
1	-1.056309090	0.790778300	-2.978156850
17	-3.403011740	0.708834390	-3.300227870
6	-1.770554680	-3.035713630	-1.276948080
1	-1.008835280	-3.127139710	-0.489774900
1	-2.758351420	-3.059828110	-0.792812340
1	-1.690834250	-3.929210480	-1.911733110
6	0.979985280	1.469829430	-0.711272330
26	1.132491580	0.699958940	1.148039170
6	0.004033430	2.052570960	0.165744950
6	-0.821616120	0.991603520	0.653662260
6	-0.676340690	-0.232280970	-0.250581360
6	0.741789430	0.059772010	-0.745079250
1	-0.052408280	3.100833210	0.449414650
1	-1.655330130	1.131801140	1.339656170
1	-0.691015820	-1.152888520	0.357695210
1	1.339862180	-0.642447630	-1.322506430
1	1.790751590	2.001202650	-1.204013450
6	2.127960900	1.793138360	2.668525750
6	3.085715940	1.193225140	1.800351190
6	2.890738560	-0.230290200	1.842428750
6	1.833899430	-0.503314840	2.761087430
6	1.337472000	0.742564290	3.247610080
1	2.005119230	2.856349170	2.852453410
1	3.826876460	1.715931940	1.202967310
1	3.462212420	-0.968335850	1.287360820
1	1.432890110	-1.485239320	2.998380700
1	0.517329570	0.874072370	3.947235820

TS

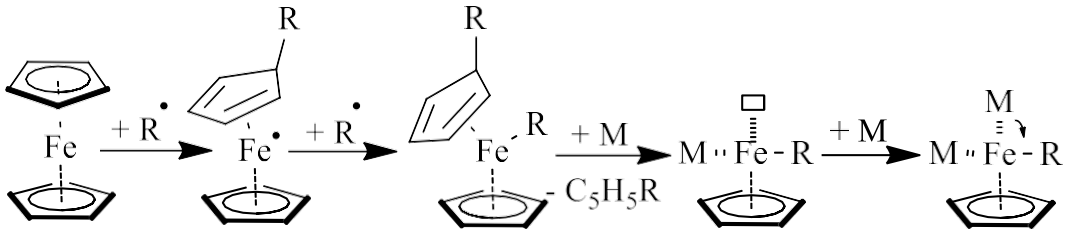
E_{total} = -2267.3520554226

Cartesian

6	-2.026959590	-0.540226920	-1.479828130
1	-2.813845260	-0.615481070	-0.722454560
6	-1.651974890	-1.825961780	-2.162583280
1	-2.315484740	-1.945919380	-3.041106180
1	-0.634756870	-1.739304350	-2.584439910
6	-2.050070360	0.691722320	-2.278057690
1	-2.196517650	1.598129420	-1.685882350
1	-1.186482490	0.798970490	-2.942367740
17	-3.520476710	0.716786080	-3.474440950
6	-1.761430850	-3.079523020	-1.289599980
1	-1.053485690	-3.061803620	-0.448586300
1	-2.774445440	-3.179888380	-0.873531140
1	-1.550726470	-3.984388690	-1.875738530
6	1.079558070	1.549064200	-0.706733090
26	1.200637150	0.765061680	1.170493540
6	0.114221440	2.161244490	0.160078730

6	-0.736787810	1.129092700	0.674158900
6	-0.418719560	-0.117112890	-0.012258930
6	0.826085180	0.138585820	-0.726794850
1	0.062010760	3.217008910	0.410964220
1	-1.564717720	1.272144460	1.362783010
1	-0.649567610	-1.087803230	0.420648770
1	1.396851720	-0.600680180	-1.281332230
1	1.885844810	2.060970320	-1.224497640
6	2.152804300	1.757677400	2.716589640
6	3.116705080	1.149043020	1.852215930
6	2.865364170	-0.264110950	1.834454370
6	1.755693560	-0.528386200	2.699526370
6	1.305026310	0.721074510	3.233728280
1	2.063716010	2.819336810	2.927405730
1	3.888681790	1.666959480	1.290671490
1	3.417177020	-1.002418500	1.259986540
1	1.310924070	-1.501468930	2.888703130
1	0.465148270	0.861605980	3.907824840

Scheme S1. Generalized scheme for the formation of a coordination AC and the polymer chain growth carried out on it in accordance with the RCP mechanism



R = $N\equiv C-C(CH_3)_2-(CH_2-CH)_2-CH_2-CH$ (n = 2)

R = $PhCH_2-CH_2-CH-CH_2Cl$ (n = 1)

M = $H_2C=CH-CH_2Cl$