Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Copolymerization of (meth)acrylates with vinyl aromatic macromonomers: understanding the mechanism of retardation on the kinetics with acrylates

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Measurement of the refractive index increment (dn.dc^{-1}) of the ASR

The refractive index increment (dn.dc^{-1}) of the ASR was measured by means of an Optilal Rex differential refractometer (RI, Wyatt. Technology) at 35 °C and using THF as the mobile phase. The experiment was carried out by injecting six samples (in the 0.5–5.0 mg.mL^{-1} concentration range) of the same batch of ASR solution. A main solution was prepared by dissolving the ASR in HPLC grade THF, (5.0 mg.mL^{-1}) and the rest five solutions (4.0, 3.0, 2.0, 1.0, and 0.5 mg.mL^{-1}) were prepared by dilution of the mother solution. The dn.dc^{-1} was calculated from the slope obtained from the plot of the refractive index against concentration. The absolute Mw for the different macromonomer:monomer ratios (0:100, 20:80, 30:70 and 40:60) were calculated taking into account the percentage of BA and ASR in the final polymer. The dn.dc^{-1} value of pBA was of 0.064 mL.g^{-1} [1]. The dn.dc^{-1} values calculated for each polymerization are presented in Table 2.

Table S1. Experimental data for the refractive index increment values (dn.dc^{-1}).

	dn.dc^{-1} (mL.g^{-1})
Macromonomer (ASR)	0.118
BA	0.064
ASR:BA 20:80	0.076
ASR:BA 30:70	0.080
ASR:BA 40:60	0.086

^{13}C NMR Spectra

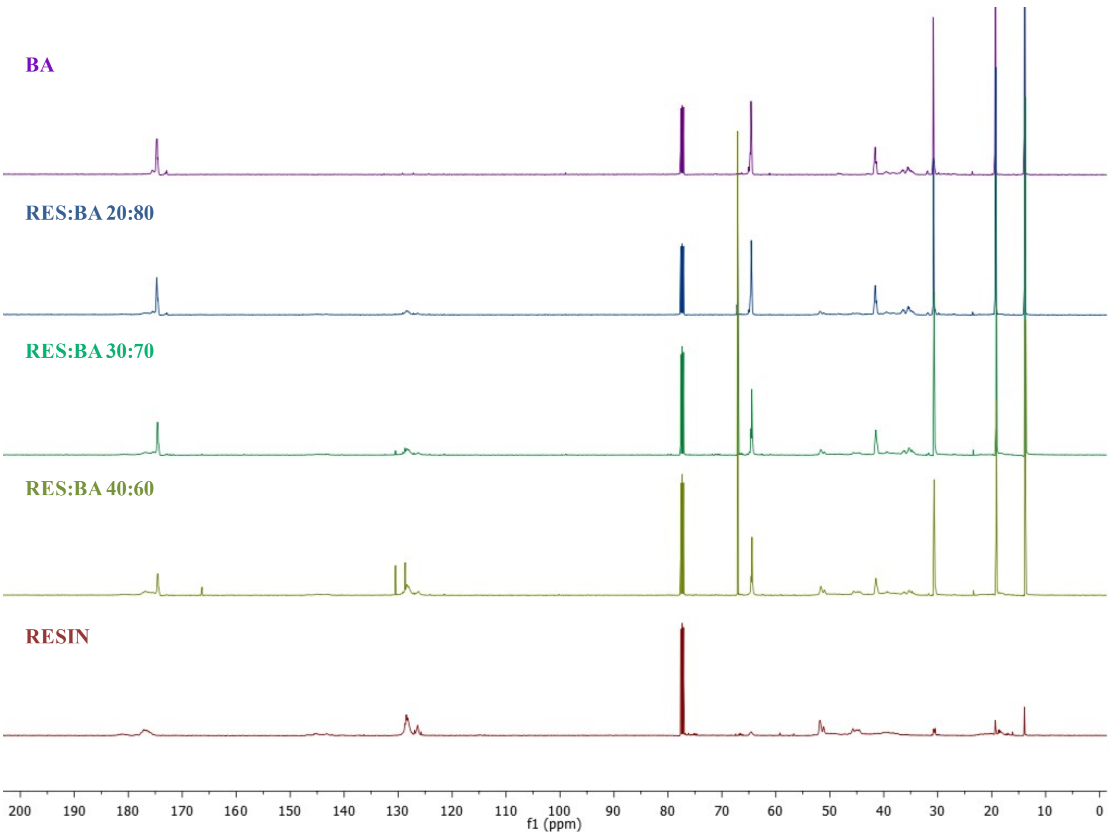

Figure S1. ^{13}C NMR spectra for the different BA polymerization and the pure ASR in $CDCl_3$.

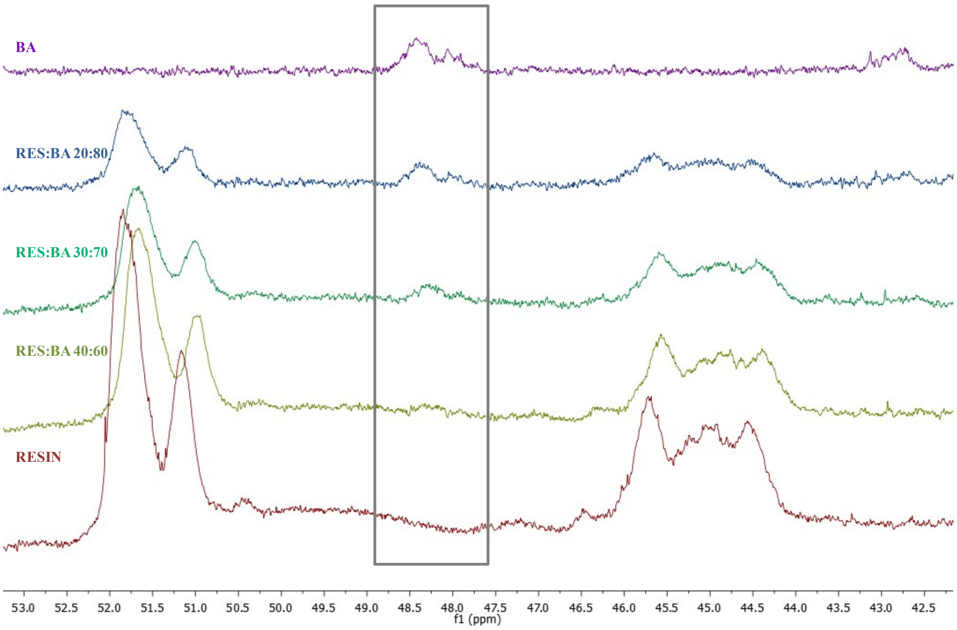

Figure S2. Zoom of the ^{13}C NMR spectra for all the polymerization and the pure ASR in $CDCl_3$.

Quantum chemical simulations

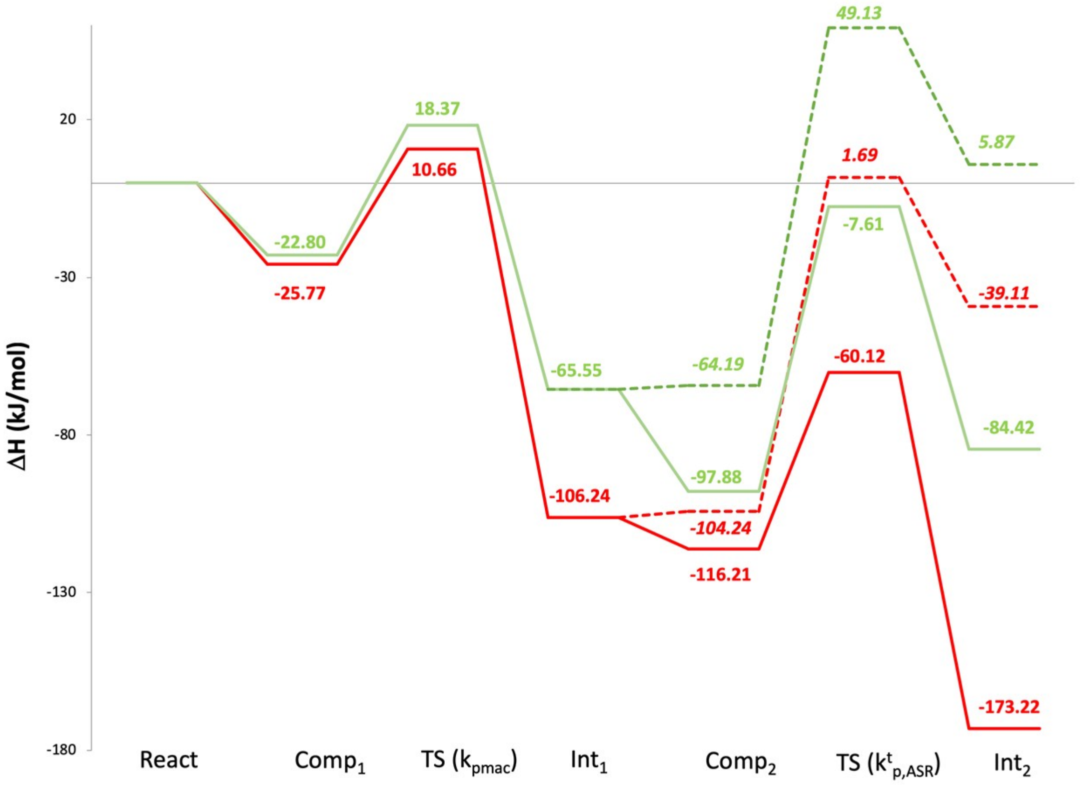

Figure S3. Potential energy surfaces corresponding to the addition of the *sec*-BA (red straight line) and BMA (green straight line) to the ASR_{ST-ST} macromonomer (Comp$_1$, TS$_1$ and Int$_1$ reaction steps), followed by the addition of the generated tertiary radicals to BA or BMA (Comp$_2$, TS$_2$ and Int$_2$ reaction steps), together with the β-scission process of the tertiary BA (dashed red line) and BMA (dashed green line) radicals, calculated at the M062X/6-311++G(2df,2p)//M062X/6-31+G(d,p) level of theory in 1,4-dioxane. Enthalpy differences in kJ mol^{-1}.

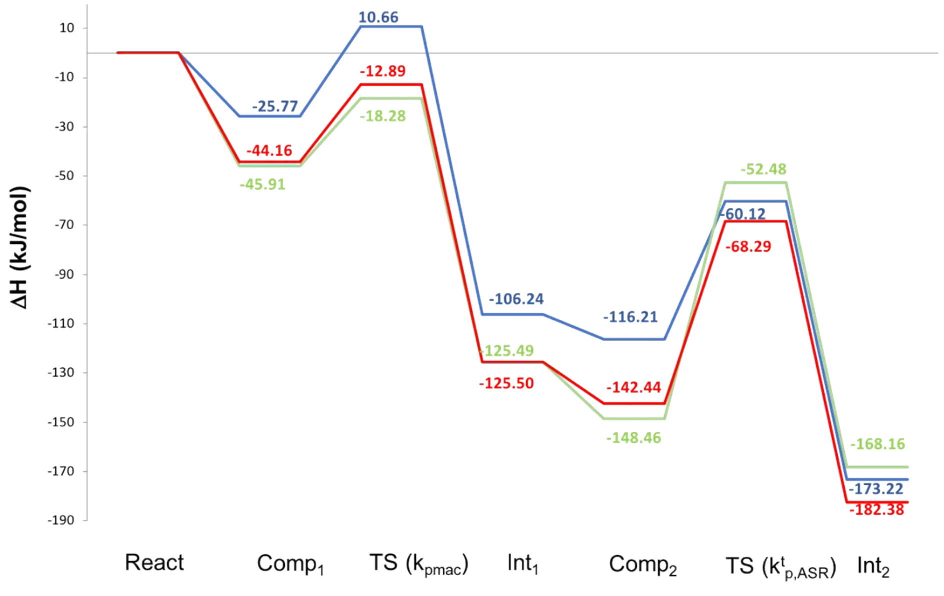

Figure S4. Potential energy surfaces corresponding to the addition of *sec*-BA to the ASR_{ST-ST} (blue line), ASR_{BA-ST} (red line) and ASR_{BMA-ST} (green line) macromonomers (Comp$_1$, TS (k$_{pmac}$) and Int$_1$ reaction steps), followed by the addition of the generated tertiary radicals to BA (Comp$_2$, TS (k$^t_{p,ASR}$) and Int$_2$ reaction steps), calculated at the M062X/6-311++G(2df,2p)//M062X/6-31+G(d,p) level of theory in 1,4-dioxane. Enthalpy differences in kJ mol^{-1}.

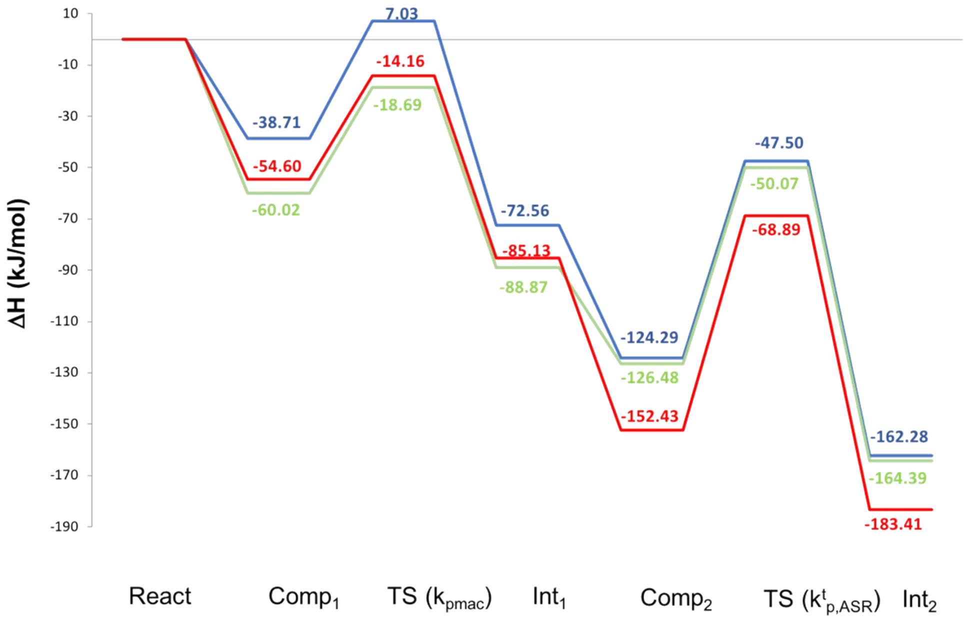

Figure S5. Potential energy surfaces corresponding to the addition of *tert*-BA to the $ASR_{ST\text{-}ST}$ (blue line), $ASR_{BA\text{-}ST}$ (red line) and $ASR_{BMA\text{-}ST}$ (green line) macromonomers (Comp$_1$, TS (k_{pmac}) and Int$_1$ reaction steps), followed by the addition of the generated tertiary radicals to BA (Comp$_2$, TS ($k^t_{p,ASR}$) and Int$_2$ reaction steps), calculated at the M062X/6-311++G(2df,2p)//M062X/6-31+G(d,p) level of theory in 1,4-dioxane. Enthalpy differences in kJ mol^{-1}.

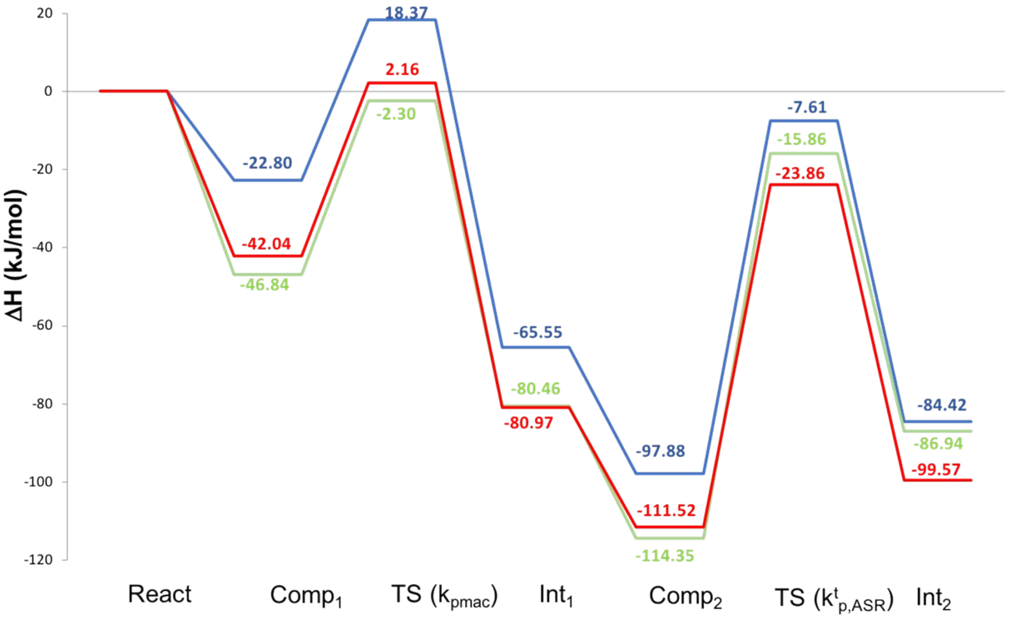

Figure S6. Potential energy surfaces corresponding to the addition of BMA to the $ASR_{ST\text{-}ST}$ (blue line), $ASR_{BA\text{-}ST}$ (red line) and $ASR_{BMA\text{-}ST}$ (green line) macromonomers (Comp$_1$, TS (k_{pmac}) and Int$_1$ reaction steps), followed by the addition of the generated tertiary radicals to BMA (Comp$_2$, TS ($k^t_{p,ASR}$) and Int$_2$ reaction steps), calculated at the M062X/6-311++G(2df,2p)//M062X/6-31+G(d,p) level of theory in 1,4-dioxane. Enthalpy differences in kJ mol^{-1}.

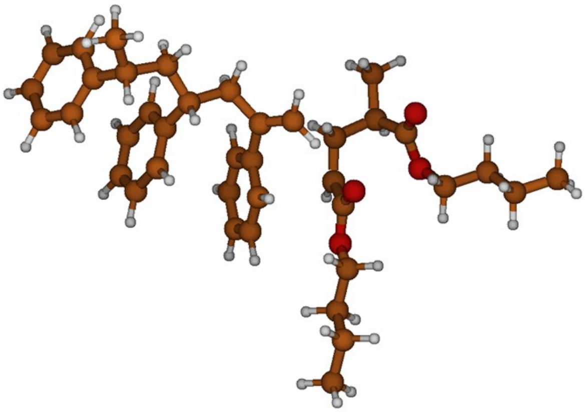

Figure S7. Molecular structure of Complex$_1$ between the *sec* -BA radical and the ASR$_{ST-ST}$ macromonomer.

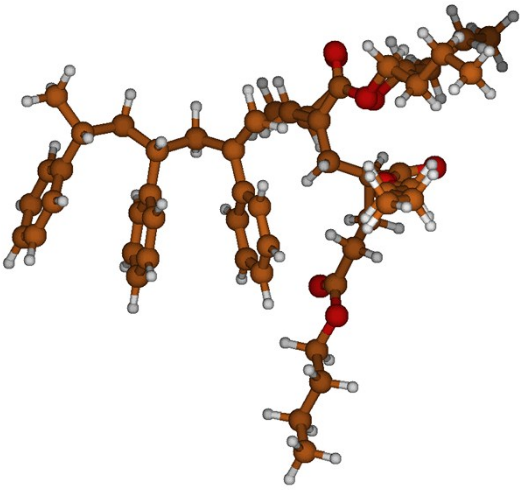

Figure S8. Molecular structure of Complex$_1$ between the *tert* -BA radical and the ASR$_{ST-ST}$ macromonomer.

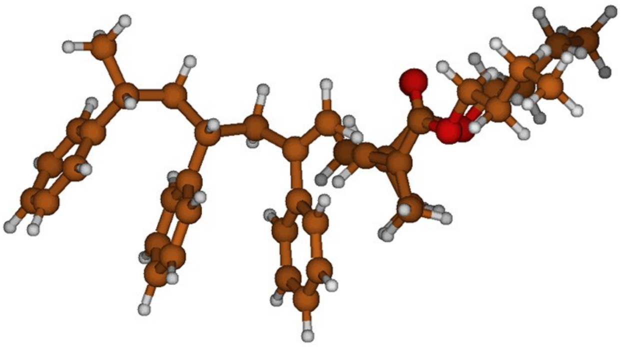

Figure S9. Molecular structure of Complex$_1$ between the BMA radical and the ASR$_{ST-ST}$ macromonomer.

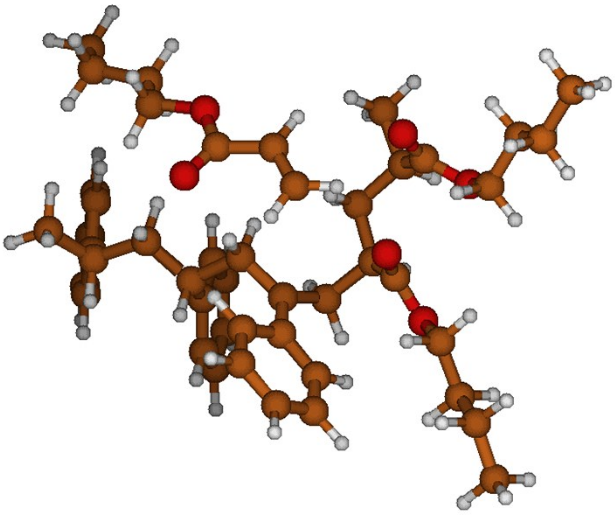

Figure S10. Molecular structure of Complex$_2$ between the tertiary radical from *sec*-BA and a BA monomer.

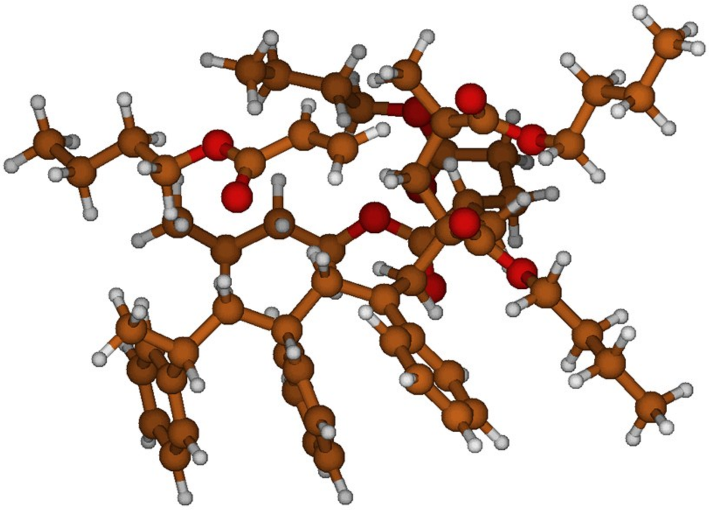

Figure S11. Molecular structure of Complex$_2$ between the tertiary radical from *tert*-BA and a BA monomer.

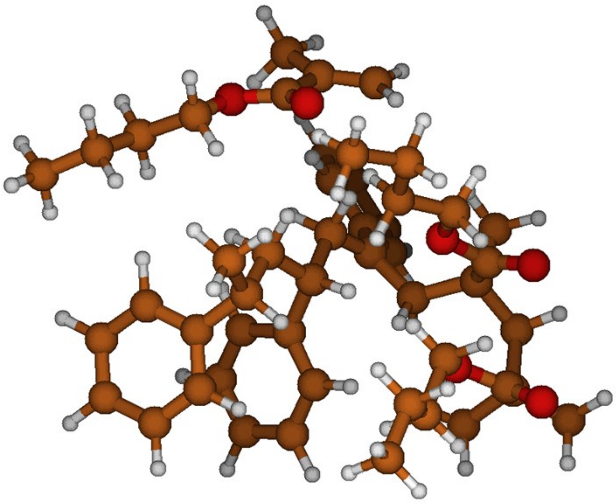

Figure S12. Molecular structure of Complex$_2$ between the tertiary radical from BMA and a BMA monomer.

Mathematical model of the semibatch solution polymerization

The simulations of the reactions with different amounts of macromonomer resin were carried out with the kinetic mechanisms described in Scheme 1 for BA and in Scheme 2 for BMA. The masses of macromonomer reported in the experimental data of solution polymerizations were reported considering the real amounts of resin used in the experiments. However, knowing that only part of the resin has a structure of macromonomer-type (61 wt%), the amounts used in the simulations were adjusted considering only the mass-fraction with terminal double bonds. Therefore the fraction without double bonds was considered as inert in the polymerization.

Kinetic reactions	Kinetic rate coefficients (Frequency factors in L mol^{-1} s^{-1} or s^{-1} and Activation energies in KJ mol^{-1})	Ref.
Initiation		
$I \xrightarrow{k_d} 2fR_0$	k_d=3.2*10^{15}exp(-131.1/RT), f=0.65	2,3
$R_0 + BA \xrightarrow{k_{iBA}} R_{i,BA}$	k_{iBA}=2.21*10^{7}exp(-17.9/RT)	4
Propagation		
$R_{i,BA} + BA \xrightarrow{k_{pBA}} R_{i+1,BA}$	k_{pBA}=2.21*10^{7}exp(-17.9/RT)	4
Chain transfer to monomer		
$R_{i,BA} + BA \xrightarrow{k_{trmBA}} P_i + R_{1,BA}$	k_{trmBA}=2.88*10^{5}exp(-32.6/RT)	5
Chain transfer to solvent		
$R_{i,BA} + S \xrightarrow{k_{trS}} P_i + R_0$	K_{trS}= 9.2 at 80 °C	This work
Backbiting		
$R_{i,3BA} \xrightarrow{k_{bb}} R^{t,BA}_{i}$	k_{bb}=3.2*10^{10}exp(-52.3/RT)	6
Chain transfer to polymer		
$R_{i,BA} + P_j \xrightarrow{k_{trp} * j} P_i + R^{t,BA}_{j}$	k_{trp}=2.48*10^{3}exp(-27.7/RT)	7
Initiation and propagation with Macromonomer		
$R_0 + ASR \xrightarrow{k_{pmac,BA}} R^{t,ASR}_{i}$ $R_{i,BA} + ASR \xrightarrow{k_{pmac,BA}} R^{t,ASR}_{i+1}$	$kp_{mac,BA}$=9.5*10^{4} at 80 °C	This work

$R^{t,BA}_{i} + ASR \xrightarrow{k_{pmac2,BA}} R^{t,ASR2}_{i+1}$	$k_{pmac2,BA} = k_{pmac,BA} \times \frac{k^{t}_{pBA}}{k_{pBA}} = 160.8$ at 80 °C	This work
Propagation of tertiary radicals		
$R^{t,BA}_{i} + BA \xrightarrow{k^{t}_{pBA}} R_{i+1,BA}$	$k_p{}^t{}_{BA}=1.58*10^6\exp(-28.9/RT)$	8
$R^{t,ASR}_{i} + BA \xrightarrow{k^{t}_{pASR,BA}} R_{i+1,BA}$	$k_p{}^t{}_{ASR,BA}=0.12$ at 80 °C	This work
$R^{t,ASR2}_{i} + BA \xrightarrow{k^{t}_{pASR2,BA}} R_{i+1,BA}$	$k_p{}^t{}_{ASR2,BA}=8.99*10^{-8}$ at 80 °C	This work
Termination		
$R_{i,BA} + R_{j,BA} \xrightarrow{cd * k_{tBA}} P_i + P_j$ $R_{i,BA} + R_{j,BA} \xrightarrow{(1-cd) * k_{tBA}} P_{i+j}$	$k_{tBA}=1.32*10^{10}\exp(-3.5/RT)$, cd=0.1	6
$R^{t,BA}_{i} + R_{j,BA} \xrightarrow{cd_{st} * k^{t}_{tBA}} P_i + P_j$ $R^{t,BA}_{i} + R_{j,BA} \xrightarrow{(1-\ cd_{st}) * k^{t}_{tBA}} P_{i+j}$ $R^{t,ASR}_{i} + R_{j,BA} \xrightarrow{cds_t * k^{t}_{tBA}} P_i + P_j$ $R^{t,ASR}_{i} + R_{j,BA} \xrightarrow{(1-cds_t) * k^{t}_{tBA}} P_{i+j}$ $R^{t,ASR2}_{i} + R_{j,BA} \xrightarrow{cds_t * k^{t}_{tBA}} P_i + P_j$ $R^{t,ASR2}_{i} + R_{j,BA} \xrightarrow{(1-cds_t) * k^{t}_{tBA}} P_{i+j}$	$k_t{}^t{}_{BA}=(\ k_{tBA*}\ k_t{}^t)^{0.5}$, $cd_{st}=0.7$	2, This work

$R^{t,ASR}_{i} + R^{t,BA}_{j} \xrightarrow{cd_t * k^t_{tBA}} P_i + P_j$ $R^{t,ASR}_{i} + R^{t,BA}_{j} \xrightarrow{(1 - cd_t) * k^t_{tBA}} P_{i+j}$ $R^{t,ASR}_{i} + R^{t,ASR}_{i} \xrightarrow{cd_t * k^t_{tBA}} P_i + P_j$ $R^{t,ASR}_{i} + R^{t,ASR}_{i} \xrightarrow{(1 - cd_t) * k^t_{tBA}} P_{i+j}$ $R^{t,BA}_{i} + R^{t,BA}_{j} \xrightarrow{cd_t * k^t_{t}} P_i + P_j$ $R^{t,BA}_{i} + R^{t,BA}_{j} \xrightarrow{(1 - cd_t) * k^t_{t}} P_{i+j}$ $R^{t,ASR2}_{i} + R^{t,BA}_{j} \xrightarrow{cd_t * k^t_{tBA}} P_i + P_j$ $R^{t,ASR2}_{i} + R^{t,BA}_{j} \xrightarrow{(1 - cd_t) * k^t_{tBA}} P_{i+j}$ $R^{t,ASR2}_{i} + R^{t,ASR}_{i} \xrightarrow{cd_t * k^t_{tBA}} P_i + P_j$ $R^{t,ASR2}_{i} + R^{t,ASR}_{i} \xrightarrow{(1 - cd_t) * k^t_{tBA}} P_{i+j}$ $R^{t,ASR2}_{i} + R^{t,ASR2}_{i} \xrightarrow{cd_t * k^t_{tBA}} P_i + P_j$ $R^{t,ASR2}_{i} + R^{t,ASR2}_{i} \xrightarrow{(1 - cd_t) * k^t_{tBA}} P_{i+j}$	k_t^t=1.29*10^7exp(-4.0/RT), cd_t=0.9	9, This work
β-scission		
$R^{t,BA}_{i} \xrightarrow{k_\beta} P_{i-j} + R_{j,BA}$	k_β=1.47*10^9exp(-55.5/RT)	6
$R^{t,ASR}_{i} \xrightarrow{k_{\beta 2}} P_{i-j} + R_{j,BA}$ $R^{t,ASR2}_{i} \xrightarrow{k_{\beta 2}} P_{i-j} + R_{j,BA}$	$k_{\beta 2}$=0.003 at 80 °C	This work

Scheme 1 Kinetic mechanism for butyl acrylate polymerization in the presence of the macromonomer. S: solvent; I: initiator; R_i: chain-end radical with length i; P_i: dead polymer with length i; $R_i^{t,BA}$: tertiary radical from BA chains; ASR: macromonomer; $R_i^{t,ASR}$: tertiary radical on ASR formed after addition of BA secondary radicals; $R_i^{t,ASR2}$: tertiary radical on ASR formed after addition of BA tertiary radicals.

Kinetic reactions	Kinetic rate coefficients (Frequency factors in L mol^{-1} s^{-1} or s^{-1} and Activation energies in KJ mol^{-1})	Ref.
Initiation		
$I \xrightarrow{k_d} 2fR_0$	k_d=3.2*10^{15}exp(-131.1/RT), f=0.65	2,3
$R_0 + BMA \xrightarrow{k_{iBMA}} R_{i,BMA}$	k_{iBMA}=3.8*10^{6}exp(-22.89/RT)	10
Propagation		
$R_{i,BMA} + BMA \xrightarrow{k_{pBMA}} R_{i+1,BMA}$	k_{pBMA}=3.8*10^{6}exp(-22.89/RT)	10
Chain transfer to monomer		
$R_{i,BMA} + BMA \xrightarrow{k_{trmBMA}} P_i + R_{1,BMA}$	k_{trmBMA}=2.82*10^{2}exp(-30.9/RT)	11
Initiation and propagation with Macromonomer		
$R_0 + ASR \xrightarrow{k_{pmac,BMA}} R^{t,ASR}_{i}$ $R_{i,BMA} + ASR \xrightarrow{k_{pmac,BMA}} R^{t,ASR}_{i+1}$	$kp_{mac,BMA}=k_{pBMA}/r_{BMA}$ r_{BMA}=0.45, reactivity ratio of BMA in copolymerization with styrene monomer	12, This work
Propagation of tertiary radicals		
$R^{t,ASR}_{i} + BMA \xrightarrow{k^{t}_{pASR,BMA}} R_{i+1,BMA}$	$k_p{}^{t}{}_{ASR,BMA}$=287 at 80 °C	This work
Termination		
$R_{i,BMA} + R_{j,BMA} \xrightarrow{cd * k_{tBMA}} P_i + P_j$ $R_{i,BMA} + R_{j,BMA} \xrightarrow{(1-cd) * k_{tBMA}} P_{i+j}$	k_{tBMA}=2.31*10^{9}exp(-10.3/RT) cd=0.65	10*
$R^{t,ASR}_{i} + R_{j,BMA} \xrightarrow{cds_t * k^{t}_{tBMA}} P_i + P_j$ $R^{t,ASR}_{i} + R_{j,BMA} \xrightarrow{(1-cds_t) * k^{t}_{tBMA}} P_{i+j}$	$k_t{}^{t}{}_{BMA}=(k_{tBMA} * k_t{}^{t})^{0.5}$, cd_{st}=0.7 $k_t{}^{t}$=1.29*10^{7}exp(-4.0/RT)	This work**
$R^{t,ASR}_{i} + R^{t,ASR}_{i} \xrightarrow{cd_t * k^{t}_{t}} P_i + P_j$ $R^{t,ASR}_{i} + R^{t,ASR}_{i} \xrightarrow{(1-cd_t) * k^{t}_{t}} P_{i+j}$	$k_t{}^{t}$=1.29*10^{7}exp(-4.0/RT), cd_t=0.9 $k_t{}^{t}$=1.29*10^{7}exp(-4.0/RT)	This work**

*The prefactor was estimated in this work using the BMA blank experiment.

**Termination rate coefficient of the ASR tertiary radical was supposed to be equal to BA tertiary radical termination rate coefficient.

Scheme 2 Kinetic mechanism for butyl methacrylate polymerization in the presence of the macromonomer. I: initiator; R_i: chain-end radical with length i; P_i: dead polymer with length i; ASR: macromonomer; $R_i^{t,ASR}$: tertiary radical on ASR formed after addition of BMA radicals.

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