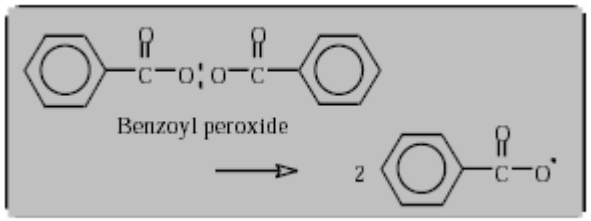
Kinetika radikalske polimerizacije

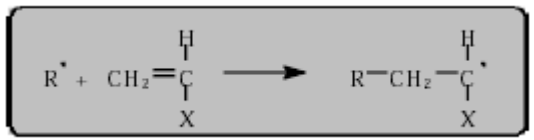
- **Iniciacija**: nastanek aktivnih centrov (prosti radikali)
- **Propagacija**: monomer reagira, veriga raste, ni nastanka novih aktivnih centrov
- **Prenos radikala**: terminacija rastoče verige, iniciacija nove verige, ni nastanka novih aktivnih centrov
- **Terminacija**: aktivni centri reagirajo med seboj, z inhibitorji, ali steno reaktorja

Iniciacija



$I_2 \xrightarrow{k_d} 2R^{\cdot}$ Decomposition

$-r_d = k_d [I]$



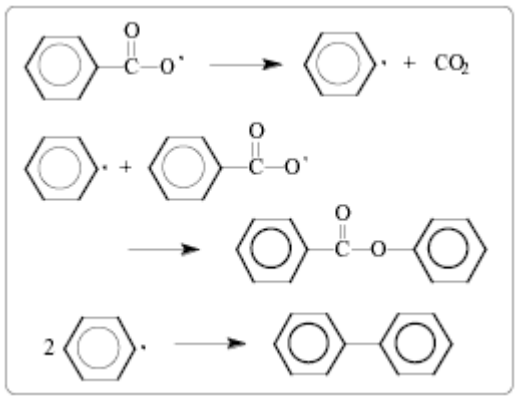
$R^{\cdot} + M \xrightarrow{k_i} M_1^{\cdot}$ Addition

$-r_i = k_i [R^{\cdot}] [M]$

Iniciator razpade, nastanejo prosti radikali,

E_a = 100 – 170 kJ/mol

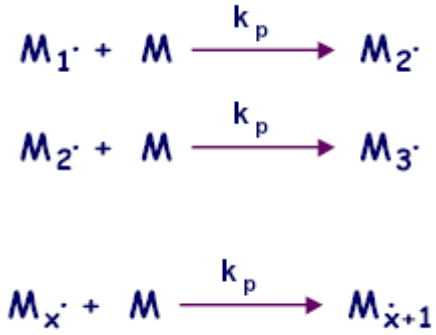
peroksidi, peroksidikarbonati, azobisizobutironitril (AIBN)



f

$-r_i = 2fk_d [I]$

Propagacija



$$-r_{p1} = k_1 [M_1^{\cdot}] [M]$$

$$-r_{p2} = k_2 [M_2^{\cdot}] [M]$$

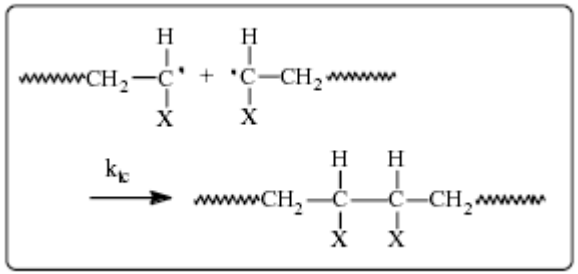
$$-r_{pN} = k_N [M_N^{\cdot}] [M]$$

$$[M^{\cdot}] = [M_1^{\cdot}] + [M_2^{\cdot}] + \ldots + [M_N^{\cdot}]$$

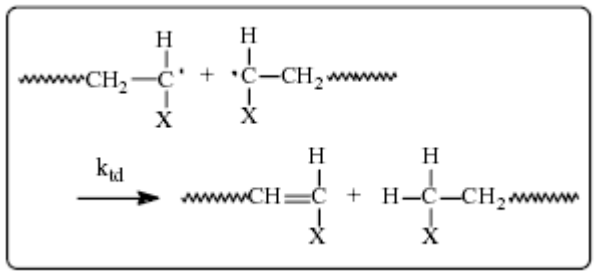
$$r_p = -\frac{d[M]}{dt} = k_p [M][M^{\cdot}]$$

k_p ~ 100-1000 L/mol s, življenjska doba rastoče verige 0.1 – 1 s =>M_W ~ 500000

Terminacija



$$M_{\dot{x}} + M_{\dot{y}} \xrightarrow{k_{tc}} M_{x+y}$$



$$M_{\dot{x}} + M_{\dot{y}} \xrightarrow{k_{td}} M_x + M_y$$

$$r_t = -\frac{d[M\cdot]}{dt} = 2\,k_t\,[M\cdot][M\cdot] \qquad k_t = k_{tc} + k_{td}$$

$k_t \sim 10^6 - 10^8$ L/mol s

$[M^{\cdot}] \sim 10^{-8} - 10^{-6}$ mol/L (steady-state approximation)

$$r_i = \frac{d[M_1^{\cdot}]}{dt} = 2 f k_d [I]$$

$$r_p = -\frac{d[M]}{dt} = k_p [M][M^{\cdot}]$$

$$r_t = -\frac{d[M^{\cdot}]}{dt} = 2 k_t [M^{\cdot}][M^{\cdot}]$$

$$[M^{\cdot}] = ?$$

Aproksimacija stacionarnega stanja

Aproksimacija stacionarnega stanja za primarni radikal

$r_{Rc} = k_d [I] - k_i [R_c^{\cdot}] [M] = 0$

Učinkovitost iniciatorja – f $\Rightarrow r_i$

Aproksimacija stacionarnega stanja za rastočo verigo

$r_{M^{\cdot}} = r_i - 2 r_t \Rightarrow [M^{\cdot}]$

Aproksimacija dolge verige (Long-Chain Approximation)

$r_M = r_i + r_p \approx r_p = k_p [M^{\cdot}] [M]$

$$[M\cdot] = \text{CONSTANT}$$

$$r_i = r_t$$

$$2f k_d [I] = 2 k_t [M\cdot]^2$$

$$[M\cdot] = \left[\frac{f k_d [I]}{k_t} \right]^{1/2}$$

$$r_p = k_p \left[\frac{f k_d [I]}{k_t} \right]^{1/2} [M]$$

$$-\frac{d[I]}{dt} = k_d [I] \qquad [I] = [I_0] e^{-k_d t}$$

$$R_p = \left[k_p \left[\frac{f k_d}{k_t} \right]^{1/2} [M] [I_0]^{1/2} \right] \left[e^{-k_d t/2} \right]$$

- Veljavnost aproksimacije stacionarnega stanja je odvisna od relativnih hitrosti iniciacije radikala in terminacije. V pretočnem reaktorju je odvisna tudi od pretoka.

Primer: CSTR

$$[M^{\bullet}] = -\frac{1}{2k_t\theta} + \sqrt{\left(\frac{1}{2k_t\theta}\right)^2 + \frac{r_i}{k_t}}$$

$$[M^{\bullet}]_{SS} = -\sqrt{\frac{r_i}{k_t}}$$

Primer: CSTR

r_i, mol/L s	θ= 1800 s		θ= 20 s	
	kt = 10^7 L/mol s	kt = 10^5 L/mol s	kt = 10^5 L/mol s	kt = 10^5 L/mol s
10^{-6}	0,9999	0,9991	0,9921	0,9240
10^{-8}	0,9991	0,9912	0,9240	0,4842
10^{-10}	0,9912	0,9160	0,4842	0,0629
10^{-12}	0,9160	0,4526	0,0629	0,0063

Konverzija

$$\frac{d[M]}{dt} = -k_p \left[\frac{fk_d[I]}{k_t}\right]^{1/2}[M]$$

$$[I] = [I_0]$$

$$[I] = [I_0]\, e^{-k_d t}$$

$$\ln \frac{[M]}{[M_0]} = -k_p \left[\frac{fk_d[I_0]}{k_t}\right]^{1/2} t$$

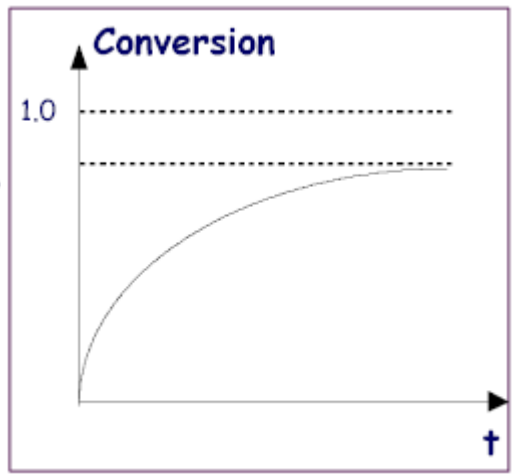
$$\ln \frac{[M]}{[M_0]} = -\frac{2k_p}{k_d}\left[\frac{fk_d[I_0]}{k_t}\right]^{1/2}\left[1 - e^{-k_d t}\right]$$

CONVERSION =

$$1 - \exp - \left\{2k_p \left[\frac{f[I_0]}{k_t k_d}^{1/2}\right]\left[1 - e^{-k_d t/2}\right]\right\}$$

MAX CONVERSION ($t \longrightarrow \infty$) =

$$1 - \exp - \left\{2k_p \left[\frac{f[I_0]}{k_t k_d}\right]^{1/2}\right\}$$



Dolžina verige

$$\nu = \frac{r_p}{2r_i}$$

$$\nu = \left(\frac{k_p}{2\left(f\, k_d\, k_t\right)^{1/2}} \right) \left(\frac{[M]}{[I]^{1/2}} \right)$$

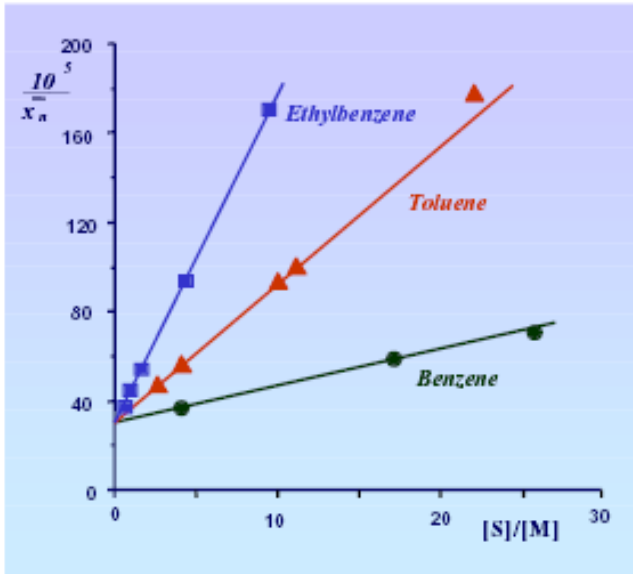
Prenos radikala

$M_N^{\cdot} + I \rightarrow P_N + I^{\cdot}$	Prenos na iniciator
$M_N^{\cdot} + M \rightarrow P_N + M^{\cdot}$	Prenos na monomer
$M_N^{\cdot} + S \rightarrow P_N + S^{\cdot}$	Prenos na topilo
$M_N^{\cdot} + P_K \rightarrow P_N + M_K^{\cdot}$	Prenos na polimer
$M_N^{\cdot} + A \rightarrow P_N + A^{\cdot}$	Prenos na "transfer agent"

Posledica prenosa na karkoli kar ni polimer je nižja povprečna molekulska masa.

$$R':H + M_x^{\cdot} \longrightarrow M\ H_x + R'^{\cdot} \qquad r_{tr} = \frac{d[M^{\cdot}]}{dt} = -k_{tr}[R':H][M^{\cdot}]$$

$$-\frac{d[M^{\cdot}]}{dt} = 2k_{td}[M^{2}\cdot] + k_{tc}[M^{2}\cdot] + k_{tr}[T][\cdot M]$$



Stopnja polimerizacije

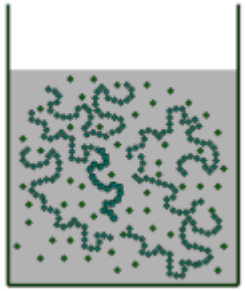
$$\overline{X}_N = 2\nu$$ kombinacija

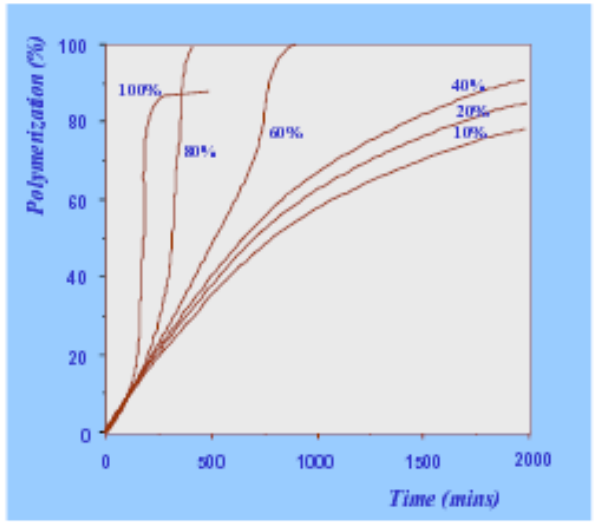
$$\overline{X}_N = \nu$$ disproporcionacija

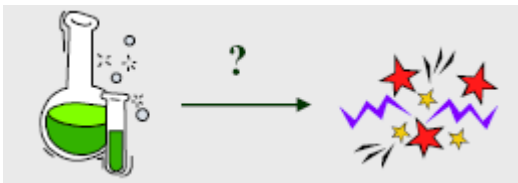
$$\overline{X}_N = \frac{\text{reagirane molekule M/L s}}{\text{nastali polimer / L s}}$$

$$\overline{X}_N = \frac{k_p [M][M^\bullet]}{k_t [M^\bullet]^2 + k_{tr,M} [M][M^\bullet] + k_{tr,S} [S][M^\bullet] + k_{tr,I} [I][M^\bullet]}$$

Trommsdorffov efekt





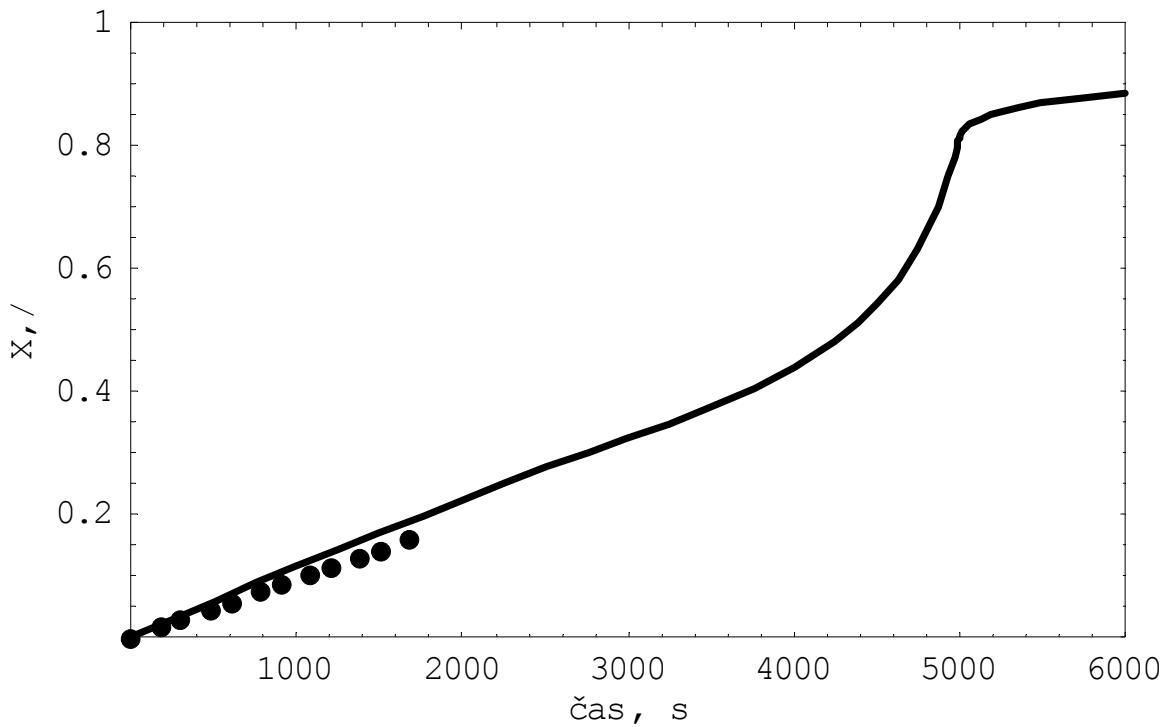


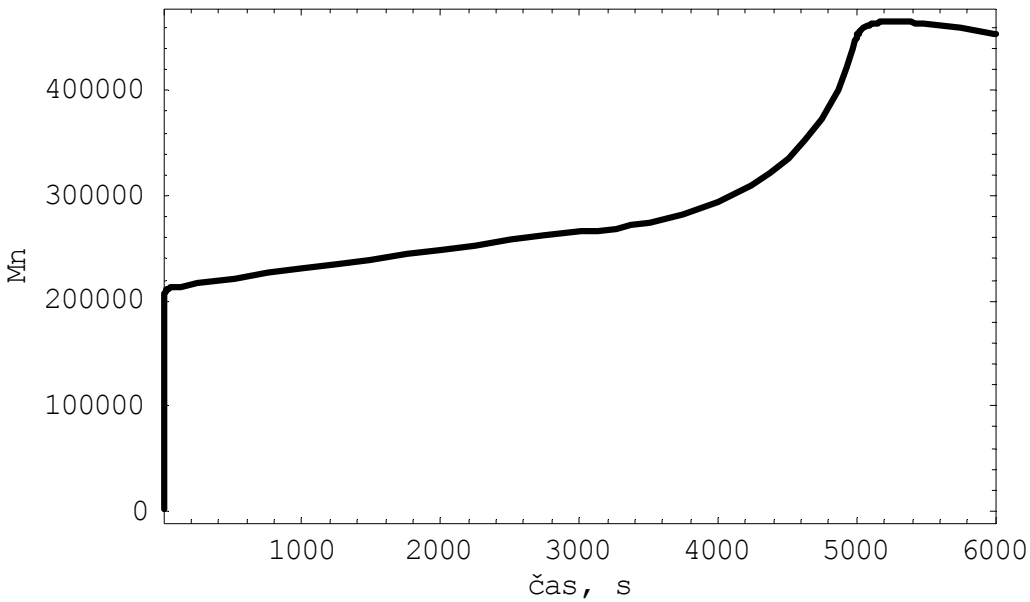
$k_p = f(X)$

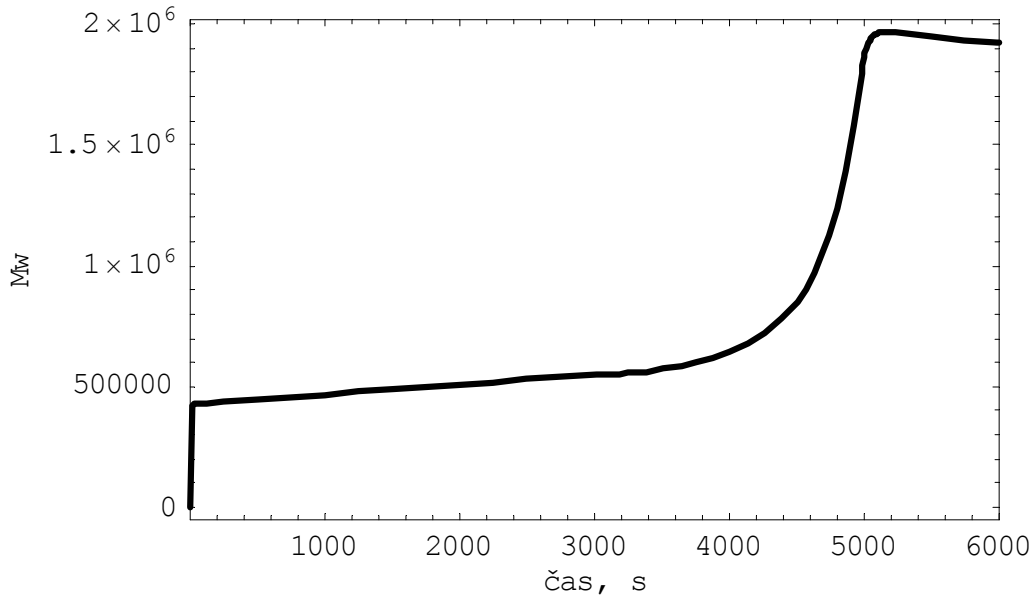
$k_t = f(X)$

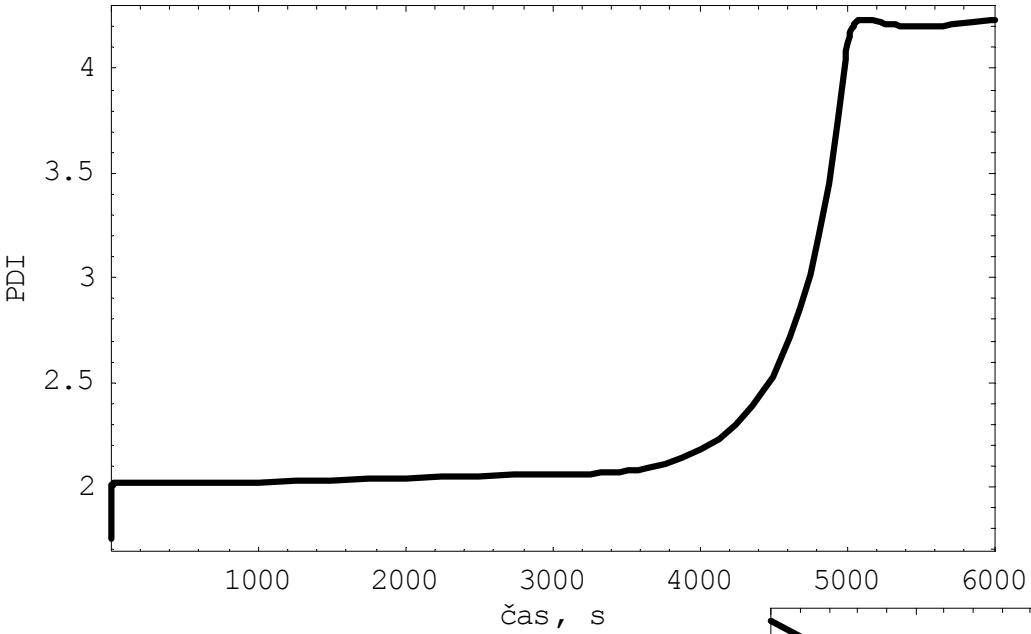
modeliranje polimerizacijskih procesov

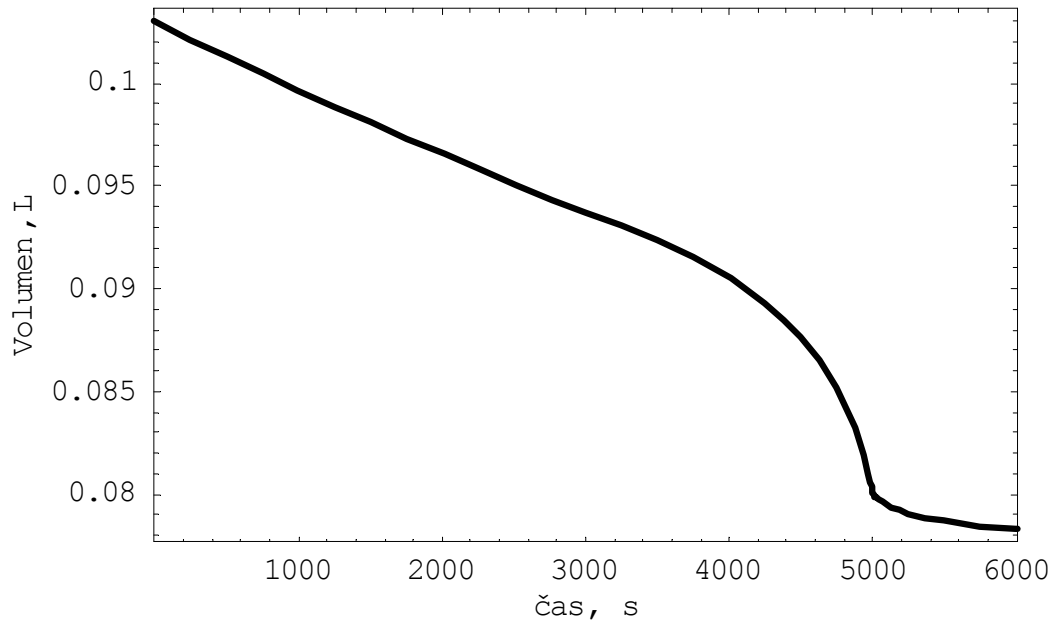
Primer:
polimerizacija metilmetakrilata v masi




Mn
400000
300000
200000
100000
0
1000
2000
3000
4000
5000
6000
čas, s


Mw
2×10^6
1.5×10^6
1×10^6
500000
0
1000
2000
3000
4000
5000
6000
čas, s


PDI
4
3.5
3
2.5
2
1000
2000
3000
4000
5000
6000
čas, s


Volumen,L
0.1
0.095
0.09
0.085
0.08
1000
2000
3000
4000
5000
6000
čas, s