Electronic Supplementary Information : Silica/methacrylate class II hybrid: Telomerisation vs. RAFT polymerisation

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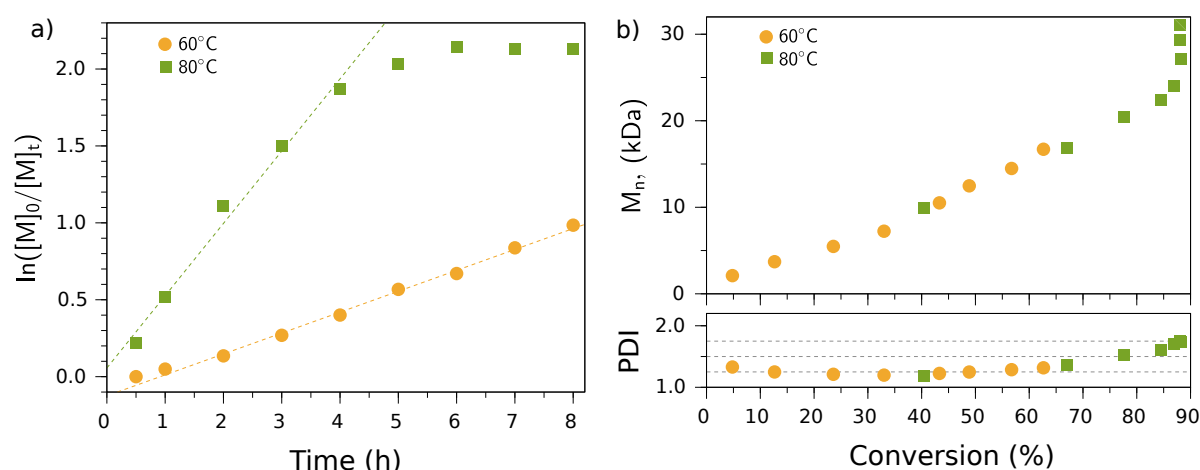
1 Characterisation data

Figure 1: RAFT polymerisation kinetic using non-distilled TMSPMA at 60°C and 80°C (Monomer/CTA/initiator=150/1/0.5, molar ratio) in toluene with a) Their kinetic plots; b) Evolution of the molecular weights and polydispersities with monomer conversion;

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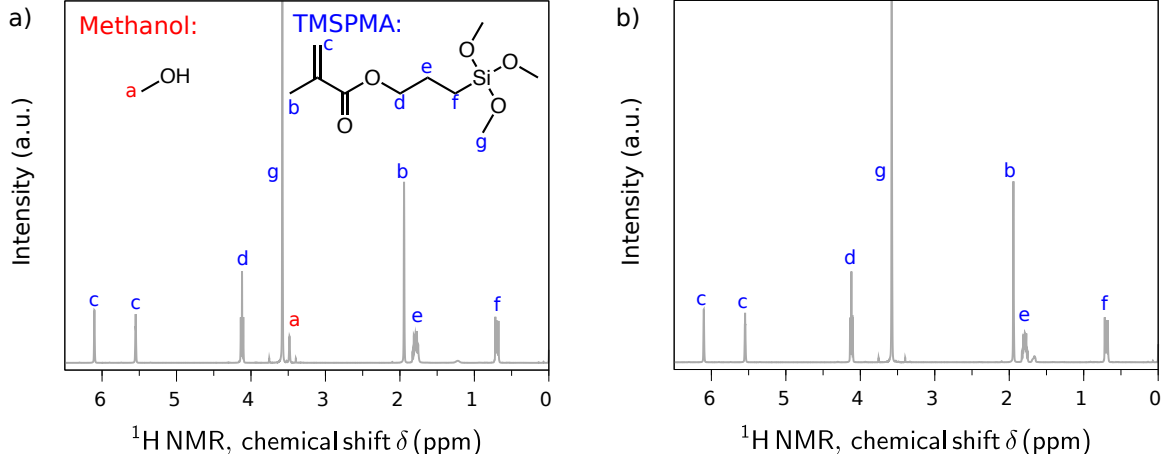
Figure 2: ^{1}H NMR of 3-(methoxysilyl)propyl methacrylate a) as received from sigma-aldrich b) after vacuum distillation against calcium hydride. Both NMR were performed in CDCl$_3$

The validity of the assumptions made in O'Brien's law was verified by showing that 1) the polymerisation of TMSPMA was occurring under stationary condition, 2) the radical propagations were not affected by the addition of the chain transfer agent.

1.1 Validity of assumptions : stationary condition

During a free radical polymerisation, the stationary condition is met when the concentration of radical is constant over time. Thus, the number of radicals formed through the thermolysis of the initiator is equalled to the number of radicals that died in the polymerisation solution. It kinetically means that rate of initiation $R_i = 2fk_d[I]$ is equal to the rate of termination $R_{te} = k_{te}[R^\bullet][R^\bullet]$. Therefore, within stationary state, the concentration of radical in the polymerisation can be written the following way :

$$[R^\bullet] = \sqrt{\frac{2fk_d}{k_{te}}[I]} \tag{1}$$

The decomposition of 2-azobisisobutyronitrile (AIBN) used here was extensively studied by Tobolsky**?**. It was found that the homolysis of AIBN follows a classic first order:
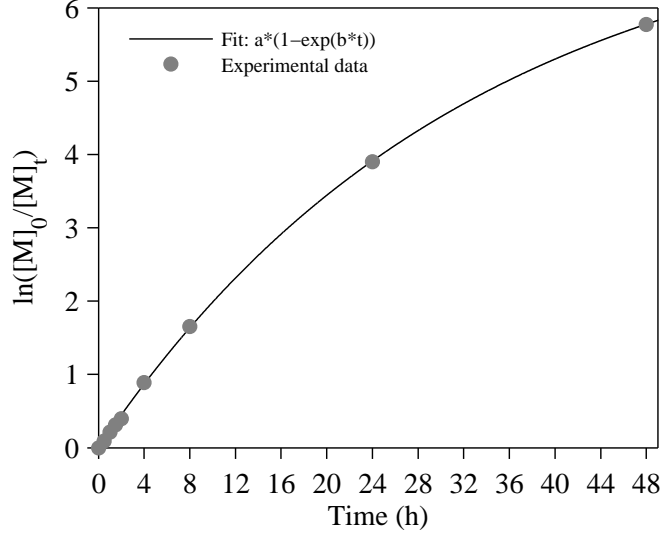
$$[I] = [I]_0 e^{k_d t} \tag{2}$$

Figure 3: Fitting of the monomer consumption during the free radical polymerisation of TM-SPMA in THF at 60^oC initiated by AIBN without chain transfer agent.

Thus, incorporating Eq. 2 & Eq. 1, in the propagation rate differential equation and after integration, the monomer concentration under stationary condition can be written in the following way:

$$\ln(\frac{[M]_0}{[M]_t}) = 2\frac{k_p}{\sqrt{k_{te}}}(\frac{f}{k_d})^{\frac{1}{2}}[I]_0^{1/2}(1 - e^{\frac{-k_dt}{2}}) \tag{3}$$

Therefore, to verify that the polymerisation of TMSPMA in THF at 60^oC was under stationary condition, the monomer consumption $\ln(\frac{[M]_0}{[M]_t})$ was followed by ^{1}H NMR over 48 hours and fitted with $a * (1 - e^{-b*t})$ as shown in Figure 3. The exponential regression appeared to match the experimental data with a correlation factor R^2=0.99, which validates the postulated assumption. From the extracted coefficient, the dissociation constant k_d of AIBN at 60^oC was calculated, giving k_d=8.56 $\pm$ 0.21 10^{-6} s^{-1}.

1.2 Validity of assumptions : propagation rate

The stationary condition having being met, the effect of the chain transfer agent on the propagation rate was investigated. As stated in equation 3, the consumption of the monomer throughout the polymerisation is directly proportional to the propagation rate, k_p. Therefore, in case of non-interaction of the chain transfer agent, the plot of
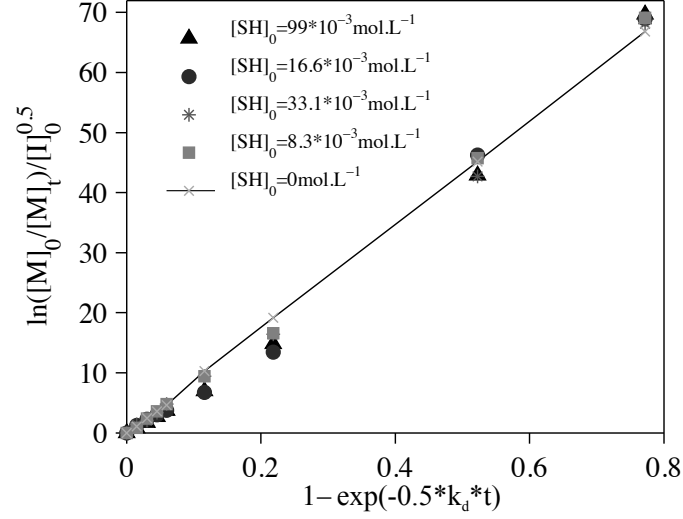
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Figure 4: Influence of the addition of thioglycerol onto the propagation rate of the free radical polymerisation of TMSPMA

$\ln\left(\frac{[M]_0}{[M]_t}\right)$ against $1 - e^{\frac{-k_d t}{2}}$ should be linear with a slope independent of the concentration of CTA. Figure 1.2 demonstrates that when thioglycerol was added ([SH] = 8.3 to 99 10^{-3} mol.L^{-1}), the propagation rate was not altered. The slopes were calculated with a maximum relative difference with conventional polymerisation of 3% given $2\frac{k_p}{\sqrt{k_{te}}}\left(\frac{f}{k_d}\right)^{\frac{1}{2}} = 89.07 \pm 1.27$. In addition, all regressions were calculated with a R$^2 \gg 0.993$.