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Thiols as chain transfer agents in free radical polymerization in aqueous solution

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Abstract

The behavior of thiophenol and aliphatic thiols of different structure as chain transfer agents in the polymerization of acrylamide and 1-vinyl-2-pyrrolidone in aqueous solution at 25 °C was studied. Addition of millimolar concentrations of thiols to acrylamide polymerization reduced notably the polymer molecular weights, without change of the polymerization rate. Measurements at different pH showed that the reactive species towards the macroradicals is the protonated −SH group. Chain transfer constants, determined from Mayo plots, are only slightly dependent on the thiol structure. Aliphatic thiols and thiophenol react at similar rates. The selectivity is opposite for acrylamide (electron acceptor) and 1-vinyl-2-pyrrolidone (electron donor), pointing to significant charge transfer contributions. The reactions rates of these sulfur compounds with the electrophilic DPPH$^{\cdot}$ radical showed higher selectivity, and are not related with the chain transfer constants measured for the acrylamide macroradicals. These results are explained in terms of the different factors that control the reactivity of thiols with macroradicals.

Keywords: Chain transfer; Aqueous polymerization; Thioles

1. Introduction

In recent years there has been renewed interest in the use of chain transfer agents to control the molecular weights of polymers obtained by free-radical polymerizations [1]. This interest is mainly due to the increased use of low molecular weight polymers. Thiols have been early employed as efficient, nearly ideal, chain transfer agents. This behavior is expected in terms of the weakness of the S–H bond [2] and the high reactivity of the thiyl radicals [3]. The first point explains the high reactivity of these compounds towards chain carrying macroradicals, leading to high chain transfer constants, irrespective of the monomer employed. The high reactivity of the thiyl radicals explains the nearly ideal chain transfer behavior of thiols, with a large decrease in the polymer molecular weight, without a significant change in the polymerization rate. Similarly, it explains why, in processes where thiols are involved in the initiation reaction, the kinetic law presents a reaction order in thiol of 0.5 [4]. Most of the works on the behavior of thiols as chain transfer agents refer to polymerization in organic media, while studies of aqueous polymerizations are scarce. Furthermore, there are very few systematic studies on the effect of the thiol structure. Early works on bulk methyl methacrylate polymerizations indicate that the chain transfer reaction for thiophenol is four-fold faster than for 2-ethanethiol [5], and chain transfer constants for phosphonated thiols are slightly dependent on the thiol structure [6]. In the present communication we report the chain transfer properties of thiophenol and several water soluble aliphatic thiols on the polymerization of acrylamide and 1-vinyl-2-pyrrolidone in aqueous solution at 25 °C.

2. Experimental part

Acrylamide from Aldrich (>99%) was used as received. 1-Vinyl-2-pyrrolidone (Merck) was purified by distillation under reduced pressure. 2,2′-Azo(2-amidinopropane) (AAPH) was purchased from Wako and used as received. All thiols were obtained from Sigma. 2,2-Diphenyl-1-picrylhydrazyl (DDPH$^{\cdot}$) was from Aldrich.

Polymerizations were carried out in degassed aqueous

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solutions at pH 6.0 and 25 °C, using the photocleavage of AAPH as radical source. The samples were irradiated in a Rayonet photochemical reactor with 360 nm fluorescent lamps for fixed periods of time. The acrylamide concentration was 0.4 M, the polymers were precipitated from methanol, and the polymerization rates (R_p) were determined gravimetrically. The 1-vinyl-2-pyrrolidone polymerization was carried out in a monomer/water (1:1) mixture. Polymerization rates were measured dilatometrically, and the polymers were isolated from the reaction mixture by dialysis against pure water and then freeze-dried. Average molecular weights were determined by viscosimetric measurements, as previously described [7].

The reactivity of the DPPH radical with thiols was measured in methanolic solutions under conditions of pseudo first-order kinetics. Deoxygenated solutions of thiols and DPPH$^{\cdot}$ were rapidly mixed and the consumption of DPPH$^{\cdot}$ was monitored at 515 nm using a Hewlett Packard 8425A diode array spectrophotometer. The initial concentrations of DPPH$^{\cdot}$ and thiols were 5×10^{-5} M and 4×10^{-4} M, respectively. Under these conditions, the back reaction can be considered as negligible [8]. Initial consumption rates were obtained from the absorbance vs. time plots.

3. Results and discussion

The addition of millimolar concentrations of thiols to the polymerization of acrylamide reduced markedly the molecular weight of the polymer. The data fit linear Mayo plots, Fig. 1. For all the sulfur compounds studied, and over all the considered range of concentrations, the rate of the polymerization process was similar to that measured in the absence of additives. These results can be explained in terms of the simple reaction scheme,

$$M_n^{\cdot} + M \rightarrow M_{n+1}^{\cdot} \qquad k_p \tag{1}$$

$$M_n^{\cdot} + RSH \rightarrow \text{polymer} + RS^{\cdot} \qquad k_{tr} \tag{2}$$

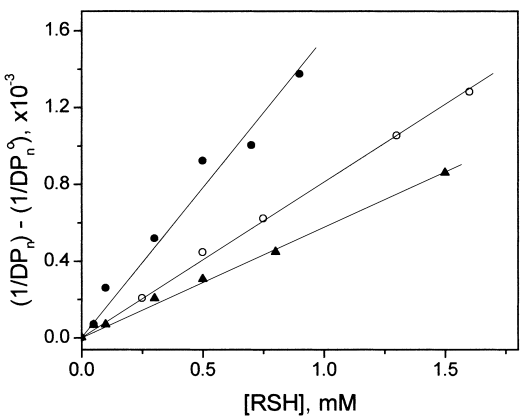

Fig. 1. Chain transfer of thiols with acrylamide: *N*-acetyl-L-cysteine (●); L-cysteine (○): penicillamine (▲). Aqueous solution at pH 6.0, 25 °C, monomer concentration 0.4 M.

$$RS^{\cdot} + M \rightarrow M^{\cdot} \tag{3}$$

In this scheme it is considered that the reactive species is the protonated thiol. The acid dissociation constants of the aliphatic sulfur compounds considered in this study lie in the 8–10 range. Hence, at pH 6.0 negligible reaction between the thiol anion and the macroradical can be expected. Since the pK_a of the aromatic thiol is much lower than those of aliphatic compounds, we determined the pK_a of thiophenol in aqueous solutions of 0.4 M acrylamide. Measurements of absorbance at 260 nm as a function of pH gave a pK_a of 6.7, that agrees with the literature value of 6.8 in bulk water [9]. In this system, polymerizations were carried out at pH 4.8. Values of chain transfer constants, C_{tr}, derived from the Mayo plots, are collected in Table 1.

Data obtained for cysteine ($pK_a = 8.3$) show that the chain transfer constant decreases two orders of magnitude when the pH is raised from 4.8 to 9.6. This decrease in reactivity cannot be related to changes in k_p, since experiments carried out in the absence of chain transfer agents showed that the polymerization rate of acrylamide does not change in the pH range 3–10. These results agree with the assumption that the reactive species towards the acrylamide macroradical is the –SH group.

For all the studied compounds, including aliphatic thiols and thiophenol, the chain transfer constants differ only by a factor three, Table 1. The differences in reactivity of aliphatic thiols could reflect the small differences in the –S–H bond energies of the investigated thiols [11]. However, other factors such as charge density and/or steric hindrance can also contribute to control the relative reactivity of these sulfur compounds towards macroradicals. It is noticeable that the lowest reactivity was found for penicillamine, the most sterically hindered compound. Otherwise, no correlation between reactivity and the hydrophility of the thiols was observed, as reported for the reaction of thiyl radicals and polyunsaturated fatty acids [12]. Probably the extended conformation of the poly(acrylamide) radical in water makes hydrophobic contributions of very little significance.

In order to evaluate the possible effect of polar structures in the transition state on the reactivity of thiols we measured the chain transfer constants of these compounds in the polymerization of 1-vinyl-2-pyrrolidine, a compound of different electron affinity. These data show somewhat different behavior from that obtained for the acrylamide. The ratio between C_{tr} of *N*-acetyl-cysteine and penicillamine is 0.18 for 1-vinyl-2-pyrrolidine and 2.8 for acrylamide. The polarity of the derived macroradicals of acrylamide and 1-vinyl-2-pyrrolidine is opposite, as deduced by the Alfrey-Price *'e'* parameter for the respective monomers. The difference observed in the relative reactivity suggests a significant contribution of charge transfer separation in the transition state.

The similar reactivity of aliphatic thiols and thiophenol presents striking differences regarding the behavior of phenols and aliphatic alcohols, where the reactivity of the

Table 1
Chain transfer constants of thiols in the polymerization of acrylamide and 1-vinyl-2-pyrrolidone, and reaction rate of thiols with DPPH· radical

Compound	C_{tr}		Relative rate DHHP[a]
	Acrylamide	1-Vinyl-2-pyrrolidone	
N-acetyl-L-cysteine	0.62	0.42	0.55
N-2-mercaptoethyl)acetamide	0.59		0.24
Glutathione	0.50		–
N-(2-mercaptopropionyl)glycine	0.47		0.34
2-Mercaptoethanol	0.47		0.24
L-Cysteine	0.34 (0.4)[b]		1
L-Cysteine pH 9.6	0.0016		–
Penicillamine	0.22	2.34	0.50
Benzenethiol	0.82		2.2

[a] Relative to L-cysteine.
[b] Ref. [10].

hydroxyl group in phenol ($C_{tr} = 6 \times 10^{-4}$) [7] is considerably higher than that of the hydroxyl group in alcohols. On the other hand, thiophenol is three order of magnitude more reactive than phenol. This difference can be ascribed to the smaller value of the bond dissociation energy of thiophenol (79.1 kcal) compared to that of phenol (91 kcal) [2].

The most surprising result is that aliphatic thiols (BDE 89 ± 1 kcal) react at similar rates to thiophenol (BDE 79.1 kcal). This can be explained in terms of the position of the critical configuration along the reaction path. Due to the large exothermicity of the process, it is expected that the critical configuration be very close to reactants. At these configurations, the factors leading to the extra stabilization afforded by the aromatic ring would not be operative. The same arguments could explain the low selectivity found for the aliphatic thiols.

To get more information on the factors that control the reactivity of macroradicals towards thiols we evaluated the reactivity of these compounds with the low reactive DPPH radical [13]. Similarly to the acrylamide macroradical, the DPPH radical is a species of high electrophilicity. Relative rates are included in Table 1. These data show some interesting results. The aromatic thiol is the more reactive sulfur compound studied, as expected from its lower BDE for the S–H bond. The reactivity of the aliphatic thiols towards the DPPH radical is slightly increased in cysteine, but there is not a clear correlation with the structure of thiol. Furthermore, it is not observed any correlation between C_{tr} values for acrylamide and the reactivity of DPPH· towards thiols. All these observations indicate that different factors control the reactivity of the hydrazyl and polyacrylamide radicals. The higher reactivity of DPPH· towards to the aromatic thiol suggests that the main factor that controls the reactivity is the dissociation energy of the –SH group, which agrees with the high exothermicity of the reaction. Meanwhile, for acrylamide macroradicals the reactivity results from the subtle interplay of charge separation at the transition state, steric hindrance, and BDE factors.

Acknowledgements

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