

# Thiophenols as chain transfer agents in the polymerization of vinyl monomers

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## Abstract

The behaviour of a series of 4-substituted thiophenols as chain transfers in the photopolymerization of the acrylamide and methyl methacrylate was studied. The addition of concentrations lower than 1 mM of thiophenols to the polymerization of acrylamide in aqueous solutions reduces slightly the polymerization rate but decreases markedly the polymer molecular weight. Chain transfer constants were determined by a modified Mayo equation that consider the variation of the polymerization rate with the chain transfer agent. The addition of thiophenols to the polymerization of methyl methacrylate in organic media reduced considerably the polymer molecular weight without variations in the polymerization rate. The chain transfer rate constants for both monomers are well correlated with the electron donor-acceptor ability of the 4-substituents, increasing with electron donating groups. An amino substituent in the 4-position increases 10 times the chain transfer constant with respect to the unsubstituted compound. No correlations were found with reported data on stability of the thiyl radicals or the addition rate to the monomer. The electron-donating effect of 4-substituents on the chain transfer constant is related to polar structures in the transition state, and suggests that the main controlling chain transfer step by thiophenols is the H-abstraction from the S–H.

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## 1. Introduction

Because of rapid growth in the field of photopolymerization, the study of free radical polymerization has attracted considerable attention in the last decades. One particular interest of these processes deals with the control of the chain length, since the final physical and mechanical properties of the polymers depend on their molecular weight. The classical method of controlling molecular weights is the addition of chain transfer agents to the polymerization medium. Thiols are well-known as efficient chain transfer for common monomers such as methyl methacrylate and styrene [1]. More recently, another interest in the reactivity of these compounds is derived from their use in thiol-ene polymerizations [2–5].

The high efficiency of thiols in the control of the chain length is expected in terms of the weakness of the S–H bond [6], and the high reactivity of the thiyl radicals towards double

bonds [7–9]. The first point explains the high reactivity of these compounds towards chain carrying macroradicals, leading to high chain transfer constants, irrespectively 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. Most of the works on the behaviour of thiols as chain transfer agents deal with aliphatic thiols, and are referred to polymerizations in organic media. In a previous work we found that water soluble aliphatic thiols are efficient chain transfer agents of the acrylamide and 1-vinyl-2-pyrrolidone polymerization in aqueous media [10]. Studies on aromatic thiols have received scarce attention. Due to the low energy of the S–H bond is expected these compounds behaviour as more efficient chain transfer agents than the aliphatic compounds. An efficient inhibition of the polymerization in the presence of 2-benzoxazolethiol and 2-benzothiazolethiol has been detected in solvent-free composition [11,12].

In this work we studied the chain transfer properties of several 4-substituted thiophenols on the polymerization of acrylamine in aqueous solutions and the methyl methacrylate in organic media. The effect of the properties of the solvent used in the polymerization composition also was analysed.

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## 2. Experimental part

Acrylamide from Aldrich (>99%) was used as received. Methyl methacrylate (MMA, Merck) was purified by distillation under reduced pressure. 4,4'-azobis(2-amidinopropane) (ABAP, Polysciences) was used without further purification. 2, 2'-Azobisisobutyronitrile (AIBN) was from Aldrich and used after crystallisation. 4-Substituted thiophenols (Aldrich) were either recrystallized or sublimed, as necessary.

Acrylamide polymerizations were carried out in degassed aqueous solutions at 25 °C, using ABAP as radical source. The acrylamide concentration was 0.4 M. Polymerizations were carried out at pH 4.6, at this pH can be considered that thiophenols are mainly as the protonated form [13]. The MMA polymerization was carried out in monomer: acetonitrile (2:1), using AIBN as photoinitiator. The samples were irradiated in a Rayonet photochemical reactor with 360 nm fluorescent lamps. The polymerization times were chosen such that conversion remained below 20%. Polymers were precipitated in methanol, and the polymerization rates ( $R_p$ ) were determined gravimetrically. Some samples were also measured dilatometrically. The intrinsic viscosity of polymers was measured in an Ubbelohde viscometer using water as solvent at 30 °C. Average molecular weights were calculated from the viscosity data using the Mark–Houwink equation

$$[\eta] = KM_n^a \quad (1)$$

With  $K=6.31 \times 10^{-3} \text{ mL g}^{-1}$  and  $a=0.8$  for acrylamide, and  $K=7 \times 10^{-3} \text{ mL g}^{-1}$  and  $a=0.71$  for methyl methacrylate [14].

## 3. Results and discussion

The irradiation of acrylamide or MMA in the presence of thiophenols and in the absence of photoinitiator did not lead to polymer, confirming that the thiophenols do not act as initiator. Charge transfer complexes as suggested for thiophenols with aromatic compounds and olefins [12,15,16] can be disregarded, since the absorption spectrum of the azo compounds used as photoinitiators remained unaltered by the presence of the thiophenols. Furthermore, spectral variations of thiols in the presence of monomers were not detected.

The addition of millimolar concentrations of 4-X-thiophenols to the free radical polymerization of acrylamide slightly reduced the polymerization rate, but decreased markedly the molecular weight of the formed polymers (Fig. 1). The decrease of polymerization rate and the molecular weight is highly dependent on the electron donor–acceptor ability of the 4-substituents, increasing with electron donating groups.

The interaction of the growing macroradicals  $M_n$  with the additive (RSH) can be represented through Eqs. (2)–(5)

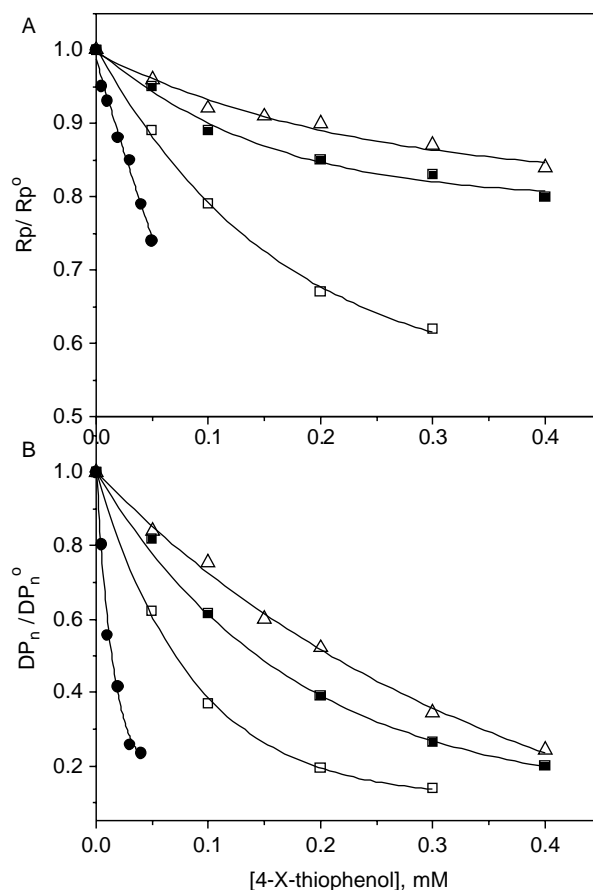
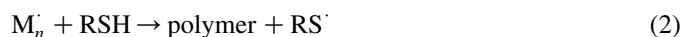


Fig. 1. Effect of the 4-substituted thiophenols on the: (A) polymerization rate of acrylamide; (B) molecular weight of poly(acrylamide): -NHCOCH<sub>3</sub> ( $\Delta$ ); -CH<sub>3</sub> ( $\blacksquare$ ); -OH ( $\square$ ); -NH<sub>2</sub> ( $\bullet$ ).



The effect of the molecular weight reduction is quantitatively given by the Mayo equation, which expresses the reciprocal of number average degree of polymerization as a function of the rates of the chain growth and the chain termination [17]. However, the use of this equation requires that polymerization rates do not depend on the presence of the chain transfer agents. To take into account the small variations of the polymerization rate with the thiophenol concentration, we used the Mayo equation as slightly modified by Lissi [18], Eq. (6)

$$\frac{1}{(DP_n)R_p} = \frac{(1 + \alpha)k_t}{2k_p^2[M]^2} + C_{tr}' \frac{[S]}{[M]R_p} \quad (6)$$

Chain transfer constants to the monomer, polymer, and initiator were omitted since they are very low for acrylamide [19], and the low photoinitiator concentrations used. Fig. 2 shows the experimental data of  $R_p$  and chain length at different concentrations of the chain transfer agents, according to Eq. (6). In these experiments the monomer concentration was constant, and the fraction of termination by disproportionation ( $\alpha$ ) can be considered as 0, then the first term at the right in Eq. (6) was considered as  $1/DP_n^0 R_p^0$ . The linearity of the plots  $1/(DP_n) R_p$  as function of  $[S]/[M] R_p$  (Fig. 2) implies that

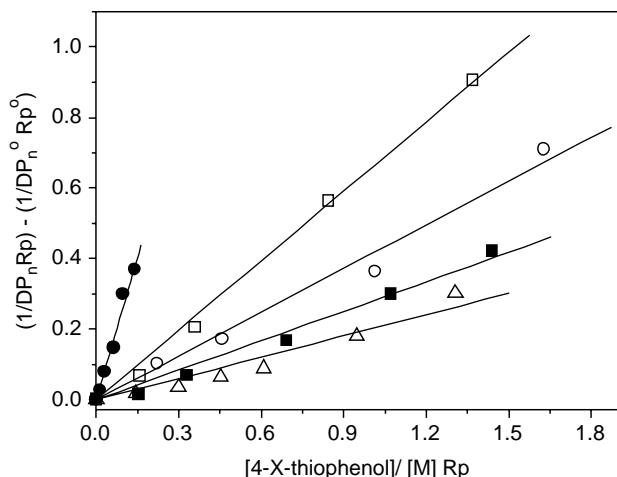


Fig. 2. Modified Mayo plots (Eq. (6)) for the determination of the chain transfer constants of 4-substituted thiophenols in acrylamide aqueous solution at pH 4.6, 25 °C.  $-\text{NHCOCH}_3$  ( $\Delta$ );  $-\text{CH}_3$  ( $\blacksquare$ );  $-\text{OCH}_3$  ( $\circ$ );  $-\text{OH}$  ( $\square$ );  $-\text{NH}_2$  ( $\bullet$ ).

the termination rate is not significantly dependent on the chain length.

In the present work, the effect of thiophenols upon the molecular weights is much higher than that on the polymerization rate ( $v_5 \gg v_6$ ), the  $C'_{\text{tr}}$  can be expressed by Eq. (7),

$$C'_{\text{tr}} = C_{\text{tr}} = \frac{k_{\text{tr}}}{k_{\text{p}}} \quad (7)$$

Values of  $C_{\text{tr}}$  and  $k_{\text{tr}}$  for several 4-substituted thiophenols, calculated from the Eq. (6) (Fig. 2), are given in Table 1. The values of  $k_{\text{tr}}$  were calculated taking  $k_{\text{p}} = 4020 \text{ M}^{-1} \text{ s}^{-1}$  at pH 4, a value measured by pulsed laser techniques [20].

Data of Table 1 show that  $k_{\text{tr}}$  is markedly dependent on the 4-substituent. The higher rate constant was obtained for the thiophenol bearing the strong electron donating amino group. Thus, a concentration as low as  $10 \mu\text{M}$  reduces the polyacrylamide molecular weight two fold. The  $C_{\text{tr}}$  value of 4-aminophenol is one order of magnitude higher than that reported for aliphatic thiols [10], compounds widely used as chain transfer agents [21,22]. The  $k_{\text{tr}}$  values are two orders of magnitude higher than those previously reported for phenols [23]. The difference in reactivity of the acrylamide macroradicals towards phenols and thiophenols can be ascribed to the smaller values of the bond dissociation energy of the thiophenol. For the thiophenol and the 4-methoxy derivative the average bond energy dissociation is  $78 \pm 1.1 \text{ kcal}$  compared to  $87.3 \pm 2.7 \text{ kcal}$  for the corresponding phenols [24].

Table 1  
Chain transfer rate constants of 4-substituted thiophenols for acrylamide polymerization in aqueous solutions pH 4.6, 25 °C

4-Substituent	$C_{\text{S}}$	$k_{\text{tr}} (\text{M}^{-1} \text{s}^{-1})$
H	0.29	1150
$\text{NHCOCH}_3$	0.20	800
$\text{CH}_3$	0.27	1090
$\text{OCH}_3$	0.41	1650
OH	0.65	2600
$\text{NH}_2$	2.7	10,900

Charge transfer effects associated with the reaction between a growing macroradical and the chain transfer agent can be quantified by the classical Hammett equation [25]

$$\log k_{\text{tr}} = \rho \sigma_{\text{P}} \quad (8)$$

In this expression, the Hammett constant ( $\sigma_{\text{P}}$ ) is characteristic of the 4-substituent, while the reaction constant  $\rho$  is characteristic of the reaction. The values of  $k_{\text{tr}}$  for acrylamide as function of the Hammett  $\sigma_{\text{P}}$  constants as depicted in Fig. 3. The thiophenols with weak electron donor substituents deviate significantly from linearity. However, excluding the phenol, the straight line is appropriated with  $\rho = -1.8$  ( $r = 0.98$ ).

The increase of  $k_{\text{tr}}$  with increasing electron donor ability indicates the presence of charge transfer structures in the transition state. This is concomitant with the increased charge density in the S–H bond as consequence of the electron donor substituents, and the electrophilic character of the acrylamide macroradicals. These polar structures could be less operative with the thiophenols bearing weak electron-donor substituents. An increase of  $k_{\text{tr}}$  with increasing electron donor ability of the 4-substituent was previously found for the polymerization of the acrylamide in the presence of phenols [23]. However, phenols showed a higher dependence of  $k_{\text{tr}}$  with the electron donor-acceptor ability of the substituents. This difference suggests that the polar nature of the transition state for the reaction of the macroradicals with phenols is higher than that of thiophenols. This can be understood considering the smaller dipole moment of S–H (3.2) compared with O–H (7.3). This means that polar effects in the transition state should be less significant for thiophenols. A mayor polar nature of the transition state of phenols with respect to thiophenols also has been proposed for the H-abstraction from these compounds by the triplet excited state of xanthene dyes [26].

Other factors as thermodynamic stability of the radicals formed after the H-abstraction could also explain the higher 4-substituent effect for phenols than thiophenols. The stability of the benzenethiyl and phenoxy radicals is increased by electron-donating substituents by delocalizing the odd electron

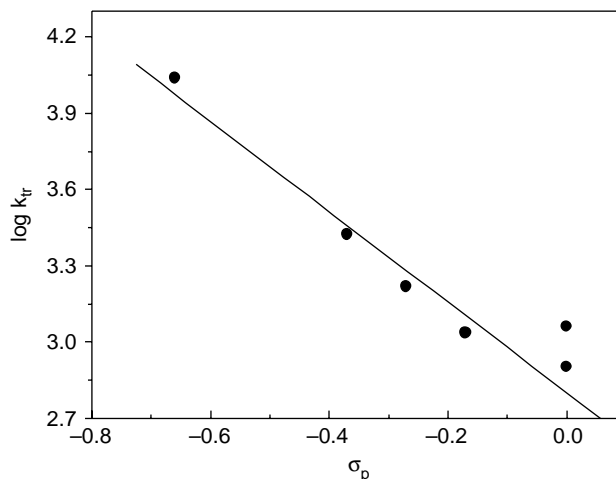


Fig. 3. Hammett plot of the chain transfer rate constant of 4-substituted thiophenols with acrylamide.

Table 2  
Chain transfer rate constants of 4-substituted thiophenols for methyl methacrylate polymerization, 25 °C

Substituent	$C_s$	$k_{tr}$ ( $M^{-1} s^{-1}$ )
4-Cl	2.8	900
H	6.0	1900
4-CH <sub>3</sub>	14	4500
4-OCH <sub>3</sub>	23.7	7580
4-OH	28	8900
4-NH <sub>2</sub>	41	13,100
2-COOCH <sub>3</sub>	0.16	51

[24]. The 4-substituted benzenethiyl radicals increase is less than a half than that for the corresponding phenoxy radicals. This is consistent with the smaller substituent effects on the reactivity of the thiophenols compared to phenols towards acrylamide macroradicals. These facts suggest that the rate of the chain transfer of thiophenols is primarily controlled by the H-abstraction from the S–H bond.

The polymerization rate of MMA remains constant with the addition of thiophenols. The molecular weight of the polymers decreases markedly in the presence of the additives. These results show that thiophenols act as chain transfer agents of MMA polymerization in acetonitrile, and reactions 3 and 4 can be considered as negligible. The chain transfer constants were determined from the experimental chain length values at different concentrations of the chain transfer agents by the classical Mayo equation, Table 2. Chain transfer to the monomer, initiator, and polymer are considered as negligible [27]. These values, obtained using  $k_p = 320 M^{-1} s^{-1}$  for MMA [28], are included in Table 2. The  $k_{tr}$  values depend on the chemical nature of the 4-substituent, correlating satisfactorily ( $r = 0.97$ ) with  $\sigma_p$ , giving  $\rho = -1.3$  (Fig. 4). The negative slope of the Hammett relation indicates the electrophilic nature of the reaction center, MMA macroradicals, with the 4-substituted thiophenols.

These plot suggests a similar mechanism to that described for the acrylamide polymerization. The

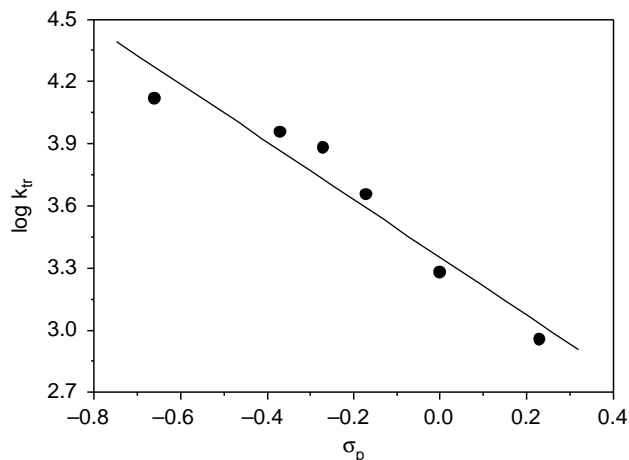


Fig. 4. Hammett plot of the chain transfer rate constant of 4-substituted thiophenols with methyl methacrylate. Monomer:acetonitrile (2:1) (v/v).

dependence of  $k_{tr}$  with the electron donor–acceptor ability of the 4-substituents is slightly lower for the MMA polymerization. Considering that the hydrogen abstraction from the S–H occurs through a mechanism that implies polar structures in the transition state, it could be expected less favourable charge transfer in the less polar medium (MMA/acetonitrile). However, the higher electrophilic character of poly(acrylamide) derived radicals with respect to those derived from MMA could be explained this difference. On the other hand, the values of  $k_{tr}$  for the same 4-substituent are higher for MMA than acrylamide, in spite of the higher electrophilic character of the acrylamide. One possible explanation of the lower  $k_{tr}$  value for acrylamide is the solvation effect of the macroradical center and/or of the –SH through intermolecular hydrogen bonding in the aqueous medium. In both cases a decreased reactivity is expected. Although intrinsic differences in the reactivity of the macroradicals cannot be disregarded.

Values of  $k_{tr}$  could increase when the dissociation energy of the S–H bond decreases. However, the decrease in  $k_{tr}$  is much higher than that expected from the energy dissociation of the S–H bond. The dissociation energy for the 4-methoxy substituted thiophenol decreases  $2.2 \text{ kcal mol}^{-1}$  with respect unsubstituted compound, but a decrease of  $9.3 \text{ kcal mol}^{-1}$  has been reported for the amino 4-substituent [24]. These differences are not reflected in the increase of  $k_{tr}$ . Further evidence on the contribution of polar structures in the transition state was obtained from the polymerization of MMA using benzene as solvent. In this case we found that the ratio of  $k_{tr}$  between 4-methoxythiophenol and 4-chlorothiophenol is 4.3. In the polar solvent acetonitrile are 9.5. The higher effect of the donor substituent (4-methoxy) in the polar solvent is indicative of the presence of polar structures in the reaction pathway.

The polymerization of MMA also was carried out in the presence of 2-COOCH<sub>3</sub> substituted thiophenol, Table 2. For this compound  $C_{tr}$  was 4 times lower than that expected from de Hammett correlation for the same substituent in the 4-position. This result cannot be due to differences in the electronic density of the S–H group since the difference in oxidation potential between 2- and 4-substituted thiophenols is  $\sim 0.05 \text{ V}$  [24]. Thus, the lower chain transfer rate constant for the 2-substituted compound indicates an important steric hindrance to the H-abstraction.

On the other hand, the efficiency of a compound as chain transfer agent also involves the rate of the addition of the radicals to the monomer double bond (reaction (5)). Ito and Matsuda [8] measured the rate constants for the addition reaction of several 4-substituted benzenethiyl radicals to MMA in cyclohexane. The rate constant is  $4.6 \times 10^5 M^{-1} s^{-1}$  for 4-methoxythiophenol, and increases one order of magnitude for the 4-chloro substituted compound. This is contrary to the substituent effects that we found on  $k_{tr}$ . This suggests that the H-abstraction from the thiol by the macroradicals must be the main pathway that controls the efficiency of thiophenols as chain transfer agents of MMA and acrylamide polymerization.

It is interesting to note that the effect of the thiophenols on the polymerization rate is significant in the polymerization of the acrylamide in aqueous solution, but is negligible for the MMA polymerization in organic medium. We also found a decrease of  $R_p$  in the polymerization of the 1-vinyl-2-pyrrolidone in the presence of thiophenol in aqueous solution. The decrease of polymerization rate in the presence of chain transfer agents indicates that the thiol derived radicals participate in termination processes (reactions (3) and (4)). Thus, the radical addition to the monomer (Eq. (5)) competes with the recombination of the radicals (Eq. (3)). This competition could result from a lower reactivity of the macroradicals ( $k_5 < k_p$ ) and/or a faster termination rate ( $k_3 > k_t$ ). Ito et al. [29] found that the rate constant for the addition of 4-aminobenzenethiyl radical to styrene is dependent on the polarity of the solvent. The rate constant decreases largely in polar solvents. This solvent effect also has to be operative for the acrylamide and could lead to a favourable competition between reactions (3) and (5). Reaction (3) inhibits the polymerization and then decreases of the polymerization rate. It is noteworthy to note that the addition of aliphatic thiols to the acrylamide polymerization in aqueous solutions does not modify the polymerization rate [10]. This suggests that the addition rate to the monomer double bond for the benzenethiyl is higher than that of aliphatic thiyl radicals. This is concomitant with the electrophilic character of the radical site in the aromatic compound.

In conclusion, thiophenols are effective chain transfer agents of the acrylamide and MMA polymerization. The chain transfer rate constants are strongly dependent on the electron donor ability of the 4-substituent. The reaction is mainly controlled by the density charge at the S–H group. The increase in charge density is reflected in the chain transfer constant and is affected by polar structures in the transition state. Changes in the polarity medium are consistent with the presence of these polar structures in the hydrogen abstraction by the macroradicals.

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