

Telomerization of acrylic acid with thioglycolic acid Effect of the solvent on the C_T value

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Summary

The telomerization of acrylic acid (AA) with thioglycolic acid (TGA) initiated with 2,2'-azobisisobutyronitrile (AIBN) was first investigated in organic medium (THF, 65°C). The kinetic study of this telomerization led to the determination of the TGA transfer constant ($C_T = 3,2$). Then, the same study was performed both in aqueous medium and in water / THF mixtures. From these works it is emphasised that the nature of the solvent plays an important role on the transfer constant. Thus, the value of C_T decreased from $C_T = 3,2$ in THF to 0,5 in water. By this way, the "ideal" case of telomerization ($CT = 1$) was reached for a mixture of solvents : water / THF (80%, 20%, v/v).

Introduction

Polyelectrolytes are polymers possessing many ionizable groups. The combination of polymeric and electrolyte behaviour gives them a number of useful properties (thickening agents, flocculants, dispersants or water softeners) (1). Polyelectrolytes may be of biological origin, like polynucleic acids, or may be synthetic like poly[(meth)acrylic acid], poly(phosphonic acid), poly(styrenesulfonic acid),...). Therefore, polymers or copolymers of acrylic acid have specific properties which open them a wide field of applications. These properties are essentially devoted to the reactivity of the carboxylic

acid, their solubility in water and to the thickening property of the low concentration alkaline solution (2).

The reactivity of these compounds allows several modifications of the polymer, that is the essential factor of the acrylic polymers applications. Thus, neutralisation with organic or inorganic bases, esterification and complexes formation with other synthetic polymers (polyethers,...) or with other macromolecular materials are of great importance.

Generally, the activity of poly(acrylic acid) depends on two factors which are molecular weight and polydispersity index of the polymer (3, 4). In the industry, the most used poly(acrylic acid) present low molecular weight and are synthesised by acrylic acid telomerization both in aqueous or organic medium.

By this way, several telogens have been used among them alkyl halides such as RCCl_3 or RCBr_3 (5-8), aliphatic mercaptans (9-14) or fluorinated mercaptans (15-16). Among these works, Pichot et al. have studied the acrylic acid (AA) telomerization in the presence of dodecanethiol as transfer agent in organic medium (isopropanol) and they have determined a C_T value equal to 2,5. In our laboratory, El Asri et al. (17) have realised a similar study for the thioglycolic acid (TGA) as transfer agent in water and they have determined a C_T value equal to 0,47.

From these two studies, it seems that the kinetic behaviour is different whether the reaction is carried out in organic medium or in aqueous medium.

Thus, we have found interesting to study, in this present article, the kinetic of the AA telomerization with TGA in organic medium (THF), in water or in mixtures of them in order to investigate the solvent effect on the transfer constant.

Experimental

(a) \square *Telomerization* : Telomerizations of acrylic acid (AA) were performed at 65°C using 2,2'-azobisisobutyronitrile (AIBN) as initiator in the presence of thioglycolic acid (TGA) as transfer agent. The solvent of telomerization is THF, water or mixtures of them. Telomerizations were carried out with distilled monomer, under a nitrogen flow and vigorous stirring.

The initial mole ratio between monomer and transfer agent ($[ATG]_0 / [AA]$) was 0,05 in all the experiments.

(b) 1H -NMR and kinetics : 1H -NMR were performed on a Bruker 200 MHz spectrometer.

During the telomerization, samples were taken directly from the mixture and quickly quenched into ice in order to stop the reaction. Monomer conversion is obtained from 1H -NMR by comparing vinylic integration of the monomer and methine integration of the polymer. Telogen conversion is determined by iodine titration.

Results and discussion

Several studies have been made in our laboratory about kinetics of telomerization reactions (18-21). We have represented in Figure 1 the mechanism of telomerization applied to AA with TGA as transfer agent.

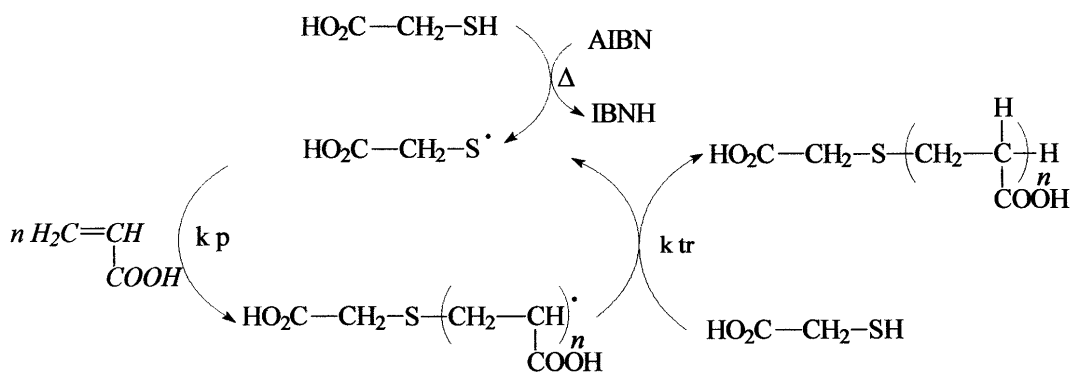


Fig. 1 : Mechanism of telomerization.

AA was telomerized at 65°C in THF with TGA as transfer agent and AIBN as initiator.

The determination of C_T value which is by definition equal to the ratio $\frac{k_{tr}}{k_p}$ is given by

O'Brien and Gornick's (22) relation :

$$\ln \frac{[ATG]_0}{[ATG]} = C_T \ln \frac{[AA]_0}{[AA]}$$

Thus, by plotting $\ln \frac{[\text{ATG}]_0}{[\text{ATG}]}$ versus $\ln \frac{[\text{AA}]_0}{[\text{AA}]}$, C_T can be determined from the slope.

Such a method was applied in our case and Figure 2 represents the straight line

$\ln \frac{[\text{ATG}]_0}{[\text{ATG}]}$ versus $\ln \frac{[\text{AA}]_0}{[\text{AA}]}$, the slope of which gives a C_T value of 3,2.

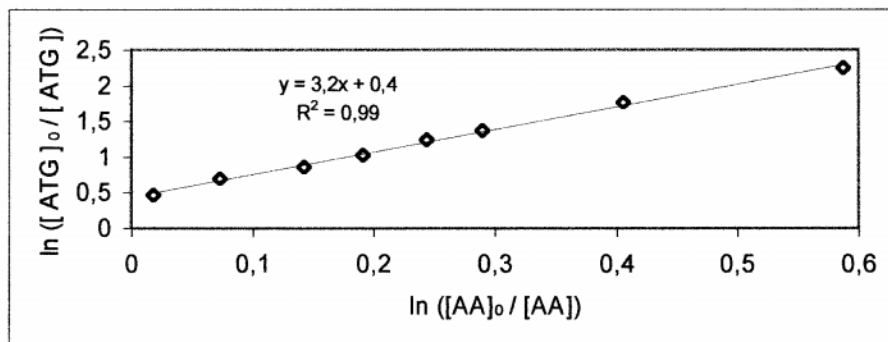


Fig. 2 : $\ln \frac{[\text{ATG}]_0}{[\text{ATG}]}$ versus $\ln \frac{[\text{AA}]_0}{[\text{AA}]}$ for telomerization of acrylic acid with thioglycolic acid at 65°C in THF.

This very high value of the transfer constant emphasises the high reactivity of the mercaptan as transfer agent and confirms the kinetics observations which show a faster consumption of the telogen than the monomer (Figure 3).

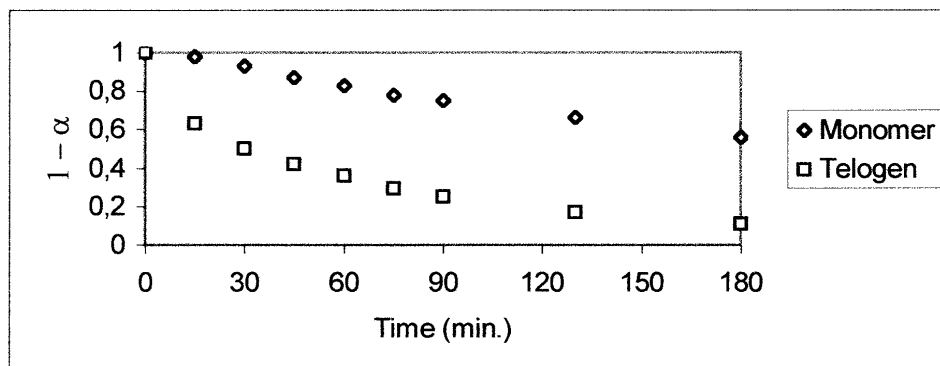


Fig. 3 : Consumption of monomer and telogen versus time for telomerization of acrylic acid with thioglycolic acid at 65°C in THF.

Pichot et al. (10, 11) have observed similar results for telomerization of AA with dodecanethiol ($C_T = 2,5$). Their value, lower than 3,2, is easily explained by the influence of the sulphur α group on the C_T value. In our case, the carboxylic group is an electron-

accepting group contrary to the aliphatic group of dodecane thiol which is an electron-donating group. Consequently, the mercapto linkage is weaker in TGA than in dodecanethiol.

As we said previously, C_T value is very high ($C_T \gg 1$) and so its interest as chain transfer agent is limited as explained by Bechkok et al. (23) for the telomerization of styrene with thioglycolic acid. In this case, the reaction leads to a complex mixture made of telomers and polymers obtained respectively at the beginning and at the end of the reaction. That is the reason why we have decided to evaluate the influence of a factor able to modify the telomerization kinetics in order to reduce the C_T value; e.g. the nature of the solvent. Many studies about solvent effect on free radical polymerization have been realized (24, 25). The monomers studied were usually of a type that exhibited solubility in both aqueous and non-aqueous solvents, allowing comparisons between solvent systems. Hydrosoluble monomers attracted a great deal of attention, due partially to their ability to undergo polymerization to high molecular weight in aqueous media, the degrees of polymerization being substantially greater than those obtained in organic media (26). This is in part due to the fact that water possesses a chain transfer constant of virtually zero (27). In addition, other factors such as the existence of polymer water interactions which produce a strongly bound hydration shell may help to protect the propagating radical centre and hinder termination (26). In other works, Kerber et al. (28-30) have studied the relative reactivity ratios of the systems styrene / acrylic acid and methyl methacrylate / acrylic acid; they showed that the r_1 , r_2 values change considerably with the used solvents.

The whole of these works brings to the fore an upper reactivity of this kind of monomer in aqueous media. Gal'Perina et al. (31) confirmed quantitatively these phenomena; their kinetic investigation showed clearly that the acrylic acid k_p value is lower in organic media than in aqueous media.

As we said previously C_T is equal to the ratio k_t / k_p ; consequently an increase of the k_p should induce a decrease of the C_T . Thus, we have applied this observation in order to follow the effect of the solvent on the C_T value. Our work was centered on the study of AA telomerization with TGA in different solvents (THF, water, THF/water mixture).

We have represented in Figure 4 the straight line $\ln \frac{[ATG]_0}{[ATG]}$ versus $\ln \frac{[AA]_0}{[AA]}$ for telomerization of AA with TGA in different solvents (THF, water, THF / water mixtures : $f_{\text{water}} = 0,1 ; 0,3 ; 0,5 ; 0,8$).

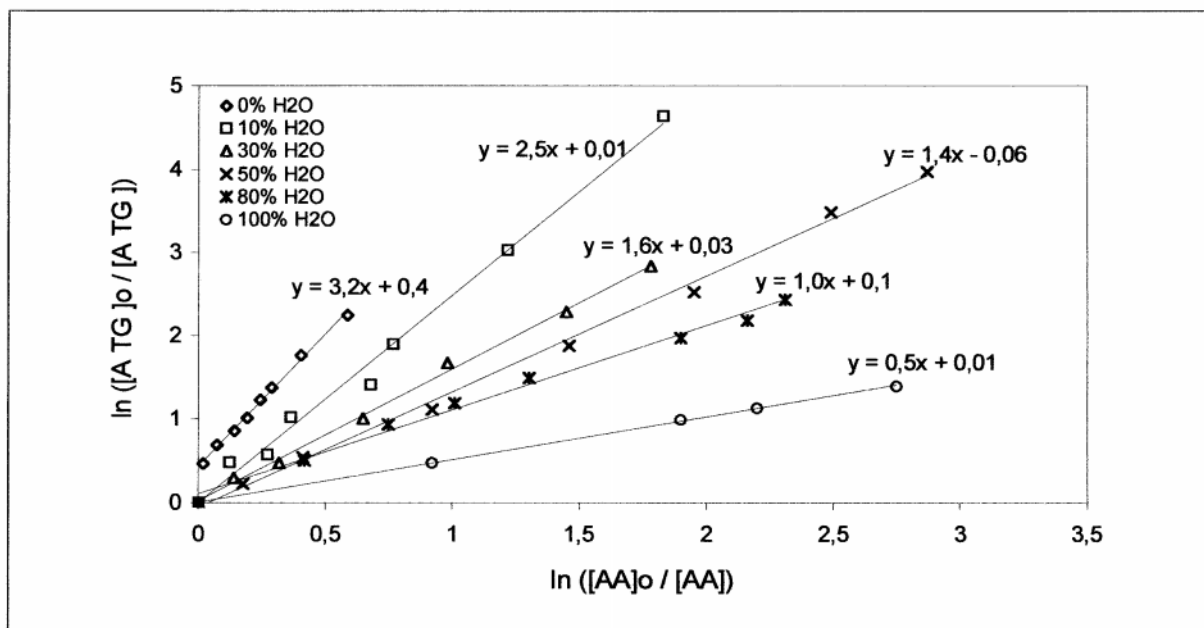


Fig. 4 : $\ln \frac{[ATG]_0}{[ATG]}$ versus $\ln \frac{[AA]_0}{[AA]}$ for telomerization of acrylic acid with thioglycolic acid at 65°C in different ratios of solvent (water / THF).

From this Figure, some observations must be done :

First, we can remark that the C_T value obtained for the telomerization in water ($C_T = 0,5$) is similar to the one obtained by El Asri (17) ($C_T = 0,49$). Moreover we have showed previously that our result in organic media ($C_T = 3,2$) is alike Pichot's result ($C_T = 2,5$). We can note particularly a continuous decrease of the C_T when the fraction of water in the solvent increases, with a minimum equal to 0,5 when the telomerization proceeds in water and an "ideal" case $C_T = 1$ for a solvent composition corresponding to 80% of water and 20% THF.

Therefore, we have observed like Gal Perina (31) an increase of the monomer consumption when the telomerization was performed in water rather than in organic media. We have also enhanced a similar consumption of both monomer and telogen for the ideal case of telomerization ($C_T = 1$) (Figure 5).

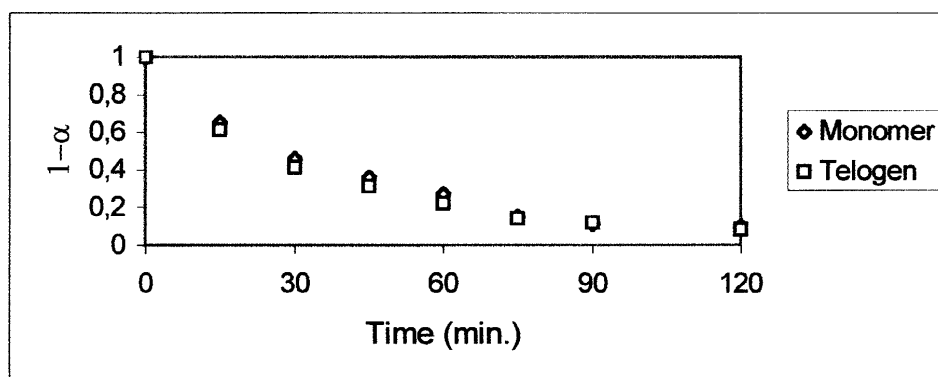


Fig. 5 : Consumption of monomer and telogen versus time for telomerization of acrylic acid with thioglycolic acid at 65°C in water / THF mixture; 80%, 20%, v/v.

Conclusion

The free radical telomerization kinetics of acrylic acid thioglycolic acid at 65°C underlined that the nature of the solvent plays an important role on the transfer constant. Thus, we showed that the value of C_T presented a decrease from $C_T = 3,2$ in THF to 0,5 in water. Furthermore, our work allowed to reach the "ideal" case of telomerization ($C_T = 1$) for a mixture of solvents : water / THF (80%, 20%, v/v).

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