

Study of the telomerization of dimethylaminoethyl methacrylate (DMAEMA) with mercaptoethanol. Application to the synthesis of a new macromonomer

Cyrille Boyer^a, Gilles Boutevin^a, Jean Jacques Robin^{b,*}, Bernard Boutevin^a

^aLaboratoire de Chimie Macromoléculaire, U.M.R. 5076, Ecole Nationale Supérieure de Chimie de Montpellier, 8, rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France

^bLaboratoire Organisation Moléculaire: Evolution et Matériaux Fluorés, UMR 5073, Université de Montpellier II-Sciences et Techniques du Languedoc-Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

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Abstract

The telomerization of dimethylaminoethyl methacrylate (DMAEMA) with mercaptoethanol initiated by 2,2'-azobisisobutyronitrile was first investigated at 70 °C and the influence of the type of solvent was studied. The results showed that well-defined telomers of DMAEMA could not be synthesized via telomerization of DMAEMA in water or water/acetonitrile mixture since the telomerization reaction is in competition with the nucleophilic addition of thiol onto the monomer. Transfer constants for mercaptoethanol in benzene and acetonitrile were determined by Mayo's and O'Brien's methods. The transfer constant obtained in acetonitrile (0,6) was higher than that obtained in benzene. This difference can be explained by the fact that the thiol was consumed by two reactions: nucleophilic addition and telomerization. The influence of solvents on the polymerization kinetics was enlightened. These results were applied to the synthesis of macromonomers of DMAEMA with isocyanatoethyl methacrylate (IEM). These macromonomers were copolymerized with styrene.

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1. Introduction

DMAEMA is an interesting monomer because the tertiary amine function allows to fix active substances onto resulting polymers. This function confers to the last chemical properties such as acido-basicity, and its hydrophilic character can be modified [1]. It is possible to use it in the elaboration of membranes [2], for biomedical applications where the adsorption or desorption of proteins is controlled by temperature changes [3,4]. Moreover, like all tertiary amines, it can be easily transformed into quaternary amines to create cation centers. The quaternary amines act as antibactericide, fungicide, flocculating agent [5,6]. Thus, the copolymers of DMAEMA/acrylamide have good

properties of complexation that have been applied in the area of waste waters treatment [7,9]. Also, these properties encouraged researches to synthesize macromonomers that can be copolymerized with other monomers in order to obtain grafted copolymers. The aim of this work has been divided into two parts: first, obtention of oligomers of DMAEMA by telomerization and synthesis of a new macromonomer of DMAEMA.

Generally, monofunctional oligomer synthesis is achieved by various methods such as atom transfer radical polymerization [10,11], or ionic polymerization [8,12]. However, these two methods present difficulties of implementation, high costs, and need high purity of the used reagents. Today, the radical polymerization remains easiest for use in the industry. In 1946, Peterson and Weber [13] and Handford [14] introduced the term of telomerization, which is defined as the reactive process where a molecule YZ, named telogen, reacts onto a polymerizable

* Corresponding author. Tel.: +33 467144304; fax: +33 467147220.
E-mail address: jrobin@univ-montp2.fr (J.J. Robin).

Table 1
Determination of elution time for the adducts $n=10-50$

DP_n	T_e^n	M_n	$\log(M_n)$	$T_e^n - T_e^{n+1}$	$\text{Log}(M_{n+1}) - \text{Log}(M_n)$
DMAEMA	23.72	157	-2.2	0	0
1 ^a	23.11	235	-2.37	0	0
2 ^a	21.96	392	-2.59	1.15	0.22
3 ^a	21.25	549	-2.74	0.71	0.15
4 ^a	20.77	706	-2.85	0.48	0.11
5 ^a	20.36	863	-2.94	0.41	0.09
6 ^a	20	1020	-3.01	0.36	0.07
7 ^a	19.69	1177	-3.07	0.31	0.06
8 ^a	19.42	1334	-3.13	0.27	0.05
10	18.96	1648	-3.22	0.22	0.04
15	18.12	2433	-3.39	0.14	0.03
20	17.55	3218	-3.51	0.1	0.02
25	17.09	4003	-3.6	0.08	0.02
30	16.72	4788	-3.68	0.07	0.01
35	16.4	5573	-3.75	0.06	0.01
40	16.12	6358	-3.8	0.05	0.01
50	15.65	7928	-3.9	0.04	0.01

^a Elution time determined experimentally.

compound M, named taxogen to form telomers of general formula $Y(M)_nZ$ with n inferior to 100. The transfer reagents can be of different nature and their choice depends on the desired properties. Moreover, all of them present an easily radically cleavable bond such as C-I [15], C-Br [16] or C-Cl [17], SH (mercaptans) [18] and P-H (phosphonate) [19]. The radical telomerization is adapted to the mono-functionalized oligomers synthesis where the telogen bears a reactive function. The telomerization of DMAEMA with thiols has not yet been studied in the literature. In a previous study [20], we showed that the tertiary amine belonging to the monomer catalyses the nucleophilic addition of SH group onto double bond in acetonitrile. This reaction involves an abnormal quantity of monoadduct. The present work reports the telomerization of DMAEMA with mercaptoethanol in order to determine the transfer constants in various solvents. First, we studied the influence of the nature of the solvent on the telomerization reaction and determined the C_T values. Second, we synthesized macromonomers starting from telomers of DMAEMA and using isocyanatoethyl methacrylate (IEM).

2. Experimental part

2.1. Chemicals

N,N-dimethyl amino ethyl methacrylate (DMAEMA) (Aldrich, 99%) and 2-mercaptoethanol (Fluka, 98%) were distilled under reduced pressure before use.

2,2'-Azobisisobutyronitrile (AIBN) was recrystallized twice from cold methanol and dried under vacuum at room temperature and stored at -4°C .

Acetonitrile (S.D.S. Society), 99.8%), benzene (SDS Society, 99.9%), CHCl_3 (SDS Society, 99%), iodine standard solution (0.1029 mol/l)(Aldrich), isocyanatoethyl

methacrylate (IEM) (Aldrich, 99%) and dibutyl tin dilaurate (DBTDL) (Aldrich, 98%) were used as received.

Deionized water was degassed before use.

2.2. Measurements

^1H NMR spectra were obtained on a BRUKER 200 MHz in CDCl_3 or DMSO as solvent. The chemical shifts were reported in parts per million with signals of traces of CDCl_3 or DMSO as internal standards.

The molecular weights were measured by SEC (Size Exclusion Chromatography) using PMMA standards (Polymer Laboratories). The chromatograms were recorded on a Spectra-Physics apparatus equipped with a pump SP 8850, a differential refractometer Spectra Physics SP 8430 RI, Phenogel columns (Mixed D, 500 Å, 100 Å) from Polymer Laboratories. THF was used as eluent at a flow rate 0,8 ml/min at 30°C .

Telomers of DMAEMA were analyzed using a calibration curve that was established starting from the first eight adducts. If we call T_e^n the elution time corresponding to each n adduct, and M_n its molecular weight, the difference ($\text{Log } M_{n+1} - \text{Log } M_n$) is proportional to the corresponding difference of elution time ($T_e^n - T_e^{n+1}$). By extrapolation of the plot ($\text{Log } M_{n+1} - \text{Log } M_n$) versus ($T_e^n - T_e^{n+1}$) to the origin we can precisely deduce the elution time of the first 50 adducts (Table 1) [18].

The DP_n was calculated using Eq. (1).

$$\bar{DP}_n = \frac{(M_n - 78)}{157} \quad (1)$$

with $M_{\text{telogen}} = 78 \text{ g/mol}$ and $M_{\text{monomer}} = 157 \text{ g/mol}$.

The FT-IR analyses were performed on a spectrometer Nicolet 510P FTIR with an accuracy $\pm 2 \text{ cm}^{-1}$.

Gas chromatography (GC) was performed on a Delsi Instruments 330 apparatus equipped with a Shimadzu

Table 2
Experimental conditions for the synthesis of different telomers from mercaptoethanol and DMAEMA in different solvents

R_0	m monomer (g)	n monomer (mol)	m telogen (g)	n telogen (mol)	m initiator (g)	V solvent ^a (ml)
0.66	7.70	0.05	2.57	0.033	0.04	50
0.33	7.70	0.05	1.28	0.016	0.04	50
0.25	7.70	0.05	0.956	0.012	0.04	50
0.20	7.70	0.05	0.78	0.01	0.04	50
0.10	7.70	0.05	0.39	0.005	0.04	50
0.05	7.70	0.05	0.195	0.0025	0.04	50

^a Acetonitrile or benzene.

C-R6A integrator and a two meter Carbowax 20 M (poly(ethylene glycol) column. Nitrogen was used as the gas vector at a pressure of 1.5 bar. The analysis was performed at an oven temperature of 150 °C. GC was used to determine the monomer conversion rate throughout the polymerization, anisole being used as internal standard.

2.3. Synthesis of monoadduct of mercaptoethanol with DMAEMA

31.4 g (0.2 mol) of DMAEMA, 15.6 g (0.2 mol) and 100 ml of acetonitrile were introduced in a round-bottom flask fitted with a condenser. The reaction was stirred and heated at 80 °C for 8 h. The solvent was evaporated to recover 44.5 g (95%) of monoadduct.

¹H NMR in DMSO: 4.8 ppm (s, 1H, OH), 3.50 ppm (m, HOCH₂CH₂), 2.3 ppm (t, 1H, CH₂CH₂S), 2.3 ppm (s, 2H, SCH₂C(CH₃)C), 0.9 ppm (s, 3H, CH₂C(CH₃)), 4.00 ppm (t, 2H, O–CH₂–CH₂), 2.3 ppm (t, 2H, –CH₂–N(CH₃)₂), 2.1 ppm (s, 6H, N(CH₃)₂).

¹³C NMR in CDCl₃: 61 ppm (HO–CH₂), 35 ppm (CH₂–S), 30 ppm (S–CH₂), 40 ppm (C(CH₃)–H), 16 ppm (CH₃), 63 ppm (COOCH₂), 57 ppm (CH₂–N), 45 ppm (N(CH₃)₂).

FT-IR analysis: 3400 cm⁻¹ alcohol band, 2900 cm⁻¹ elongation C–H, 1730 cm⁻¹ carbonyl group, 1150 cm⁻¹ tertiary amine.

2.4. Synthesis and kinetics of telomerization reaction of mercaptoethanol with DMAEMA

Different telomerizations have been performed in acetonitrile and benzene with different molar ratio R_0 ($R_0 = n_{\text{telogen}}/n_{\text{monomer}}$) from 0.66 to 0.05. The quantities of reagents are summarized in Table 2. As an example, for $R_0 = 4$, in a 50 ml flask were introduced 7.7 g (0.05 mol) of monomer, 0.956 g (0.0123 mol) of mercaptoethanol, 0.04 g ($2.45 \cdot 10^{-4}$ mol) of 2,2'-azobisisobutyronitrile (AIBN) ($C_0 = n_{\text{initiator}}/n_{\text{monomer}} = 0.5\%$) and the solution was diluted to 50 ml with benzene or acetonitrile. The solution was bubbled with argon for 20 min before heating 14 h at 70 °C. The solution was then cooled to room temperature. The solvent and the excess of telogen were removed under reduced pressure. The telomer was precipitated in hexane, filtered and dried under vacuum. The telomers appeared as a

viscous orange liquid (yield 90%). Cumulated $\overline{DP}_n^{\text{cum}}$ was determined using ¹H NMR, FT-IR and SEC.

FT-IR analysis: 3400 cm⁻¹ alcohol band, 2900 cm⁻¹ C–H elongation, 1730 cm⁻¹ carbonyl group, 1150 cm⁻¹ tertiary amine.

2.5. Telomerization kinetics

All the kinetics have been studied following the monomer and telogen concentrations versus time reaction. Each reaction was monitored by sampling and each aliquot was quenched in ice in order to stop the reaction. Different analytical methods have been used to quantify monomer conversion like ¹H NMR and gas chromatography (GC). The monomer consumption was calculated by GC using the signal of solvent as internal reference.

The thiol conversion of each sample was evaluated using titration of SH group with a 0.002 mol/l iodine solution prepared from iodine standard solution (0.1029 mol/l). The thiol concentration ([RSH]) versus time is given by the following equation:

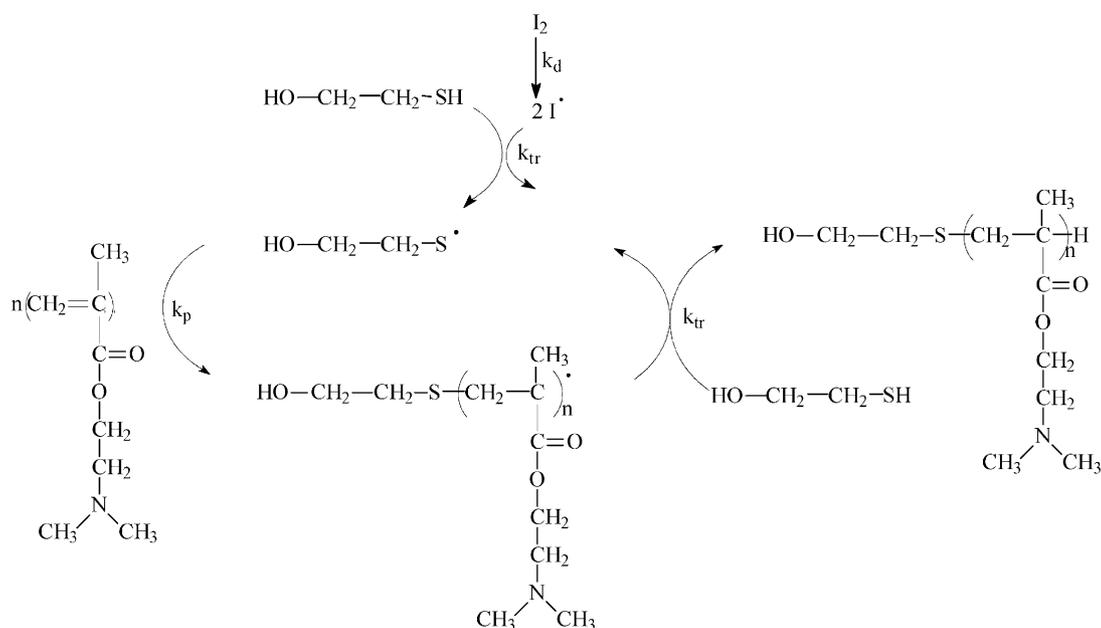
$$[\text{RSH}]_t = V_{\text{eq}} \frac{[I_2]_0}{V_{\text{eq}(0)}} \quad (2)$$

where $V_{\text{eq}(0)}$ and V_{eq} are, respectively, equivalent to the volume at $t=0$ and at t ; $[\text{RSH}]_t$ and $[I_2]_0$ are, respectively, the thiol concentration at different time and the iodine concentration at $t=0$.

2.6. Functionalization of monoadduct and telomers by isocyanatoethyl methacrylate (IEM)

5 g (0.022 mol) of monoadduct were dissolved in 200 ml of toluene and dried by azeotropic distillation using a Dean Stark vessel for 6 h at 130 °C. The temperature was then decreased to 60 °C, and 3.41 g (0.022 mol) of IEM with 0.1 wt% with respect to telomers of dibutyl tin dilaurate (DBTDL) was added using a syringe. The reaction was carried out for 6 h at 60 °C, and afterwards, the toluene was evaporated under reduced pressure. The functionalized telomer appeared as a viscous orange liquid.

10 g (0.0154 mol, 650 g/mol) of telomer were dissolved in 200 ml of toluene, following the experimental procedure described above, and 2.40 g (0.0155 mol) of IEM with



Scheme 1. Reactional mechanism of the radical telomerization reaction.

0.1 wt%. DBTDL were added. Kinetics of the reaction were estimated by FT-IR in solvent and non reacted IEM was evaporated under reduced pressure. The macromonomer was precipitated in hexane.

2.7. Copolymerization of macromonomer with styrene

Macromonomers presenting different molecular weights obtained according to the previous syntheses were tested in copolymerization with styrene to evaluate their reactivities. The molar ratio of macromonomer to styrene in the initial mixture was fixed at 10%.

10 g (0.1 mol) of styrene, 8.0 g (0.010 mol) of macromonomer ($\bar{M}_n = 800$ g/mol) of DMAEMA and 0.088 g (0.0005 mol) of AIBN ($C_o = 0.5\%$) were introduced in 25 g of acetonitrile. The mixture was degassed for 15 min with argon. Then, the mixture was heated at 70 °C for 14 h. The copolymer obtained was precipitated in water and analyzed by ^1H NMR and FT-IR (Fourier Transformed Infrared). The same procedure was followed for the synthesis of all the copolymers.

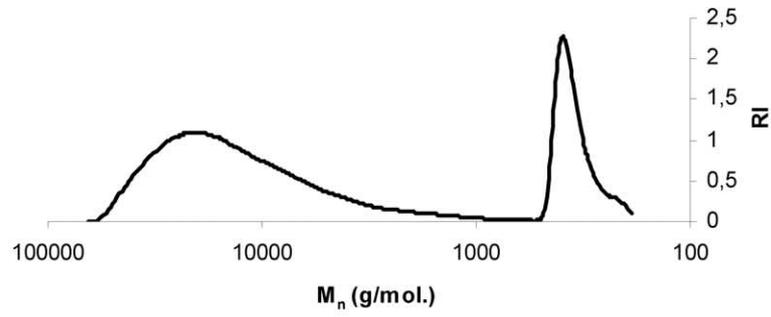
3. Results and discussion

Telomerization is an easy method to obtain monofunctional oligomers [21–23] in favoring transfer reactions [24, 25] (Scheme 1). In a previous paper, we highlighted the telomerization of DMAEMA [20] with mercaptoethanol in acetonitrile, and showed that a part of thiol is consumed by nucleophilic addition of the thiol onto the monomer.

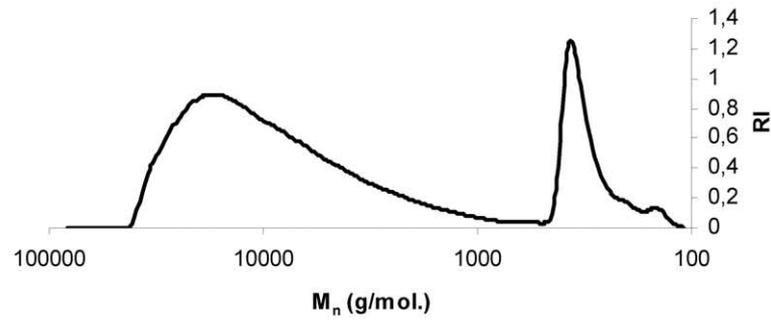
3.1. Effect of solvent on the molecular weight distribution obtained by SEC analysis

Many kinetical studies concerning the influence of the solvent in radical polymerization have been carried out previously. These studies highlighted that the solvent could present interactions with the macroradical, and could slow down the polymerization rate and therefore could influence the molecular weights of the obtained telomers. For example, Destarac [26] and Bauduin [27] studied the telomerization of vinyl acetate with chloroform as telogen agent in different solvent (benzene or acetonitrile). They showed that the solvent nature has an effect on the C_T value and the molecular weight distributions were affected when using benzene or acetonitrile. Indeed, in benzene, the reaction is slowed down by the presence of a intermediary reaction [28], and C_T value in benzene is higher than in acetonitrile. Other studies showed that the telomerization of acrylic acid could be influenced by the nature of the solvent [29,30]. For example, the telomerization of acrylic acid depends on the nature of the solvent (THF or water). The C_T value are higher in presence of water than in THF. These variations are due to a reduction of k_p in the different used solvents, what implies different $\bar{D}P_n$ [31]. We decided to study the influence of the nature of the solvent on the telomerization of DMAEMA. As we observed previously [20], the telomerization of DMAEMA in acetonitrile involves the formation of a great quantity of monoadduct. This quantity of monoadduct is prejudicial because it involves a strong increase in the I_p (polydispersity index) due to a mixture of polymer and monoadduct.

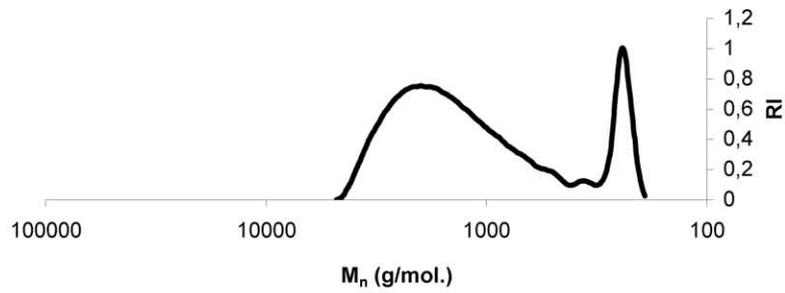
The telomerizations were carried out at 70 °C under the same conditions of concentration of monomer (DMAEMA),



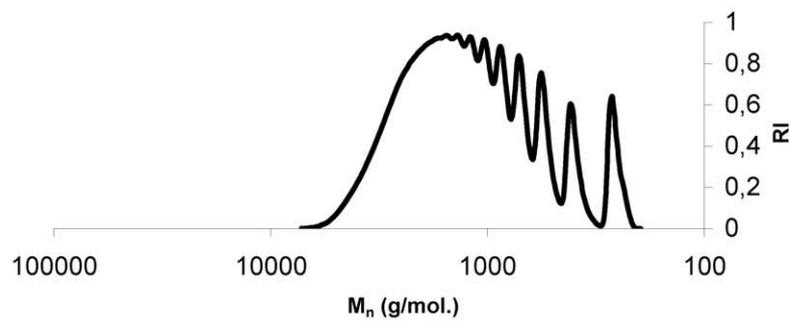
a: in water



b: in water/acetonitrile mixture (v. 75/25%).



c: in acetonitrile.



d: in benzene.

Fig. 1. SEC chromatogram analysis of telomers of DMAEMA in different solvents.

Table 3
Comparison of molecular weight and the I_p according to the solvent

$[R_0]$	Solvents	\bar{M}_n^*	\bar{M}_n^{theo}	I_p	Figures
0.2	Water	1150	860	11.5	1(a)
0.2	Water (25 vol%)/acetonitrile(75 vol%)	1100	860	11.3	1(b)
0.2	Acetonitrile	900	860	2.40	1(c)
0.2	Benzene	860	860	1.6	1(d)

$[T]=0.202$ mol/l, $[M]=1$ mol/l, $[AIBN]=0.0050$ mol/l. \bar{M}_n^* determined by SEC, \bar{M}_n^{theo} theoretical molecular weight calculated according to Eqs. (1) and (3).

telogen (mercaptoethanol) and in the presence of AIBN as initiator. We used 4 types of solvents: water, water–acetonitrile mixture (25–75 vol%), acetonitrile, and benzene. The first telomerization was achieved in water, which presents a transfer constant equal to zero according to Dainton et al. [32,33]. In these conditions, we observed by SEC analysis an increase in the formation of monoadduct and in the same time, the formation of polymer (Fig. 1(a)). So, it appears that the quantity of monoadduct increases with the polarity of solvent, thus we decided to replace water by a non-polar solvent such as benzene.

Theoretical \bar{DP}_n^f was calculated according to Eq. (3) which is valid only for a conversion rate close to 1 whatever

is C_T value:

$$\bar{DP}_n^f = \frac{1}{R_0} \quad (3)$$

where R_0 is the ratio [monomer]/[telogen].

In Table 3, the molecular weights, measured by SEC, are summarized. These molecular weights correspond to a monomer conversion rate of about 90% (measured by GC) and are close to the ones calculated with Eq. (3).

However, the polydispersity indexes (I_p) are different according to the nature of the solvent:

- Water used as solvent gives very high I_p , characteristic of

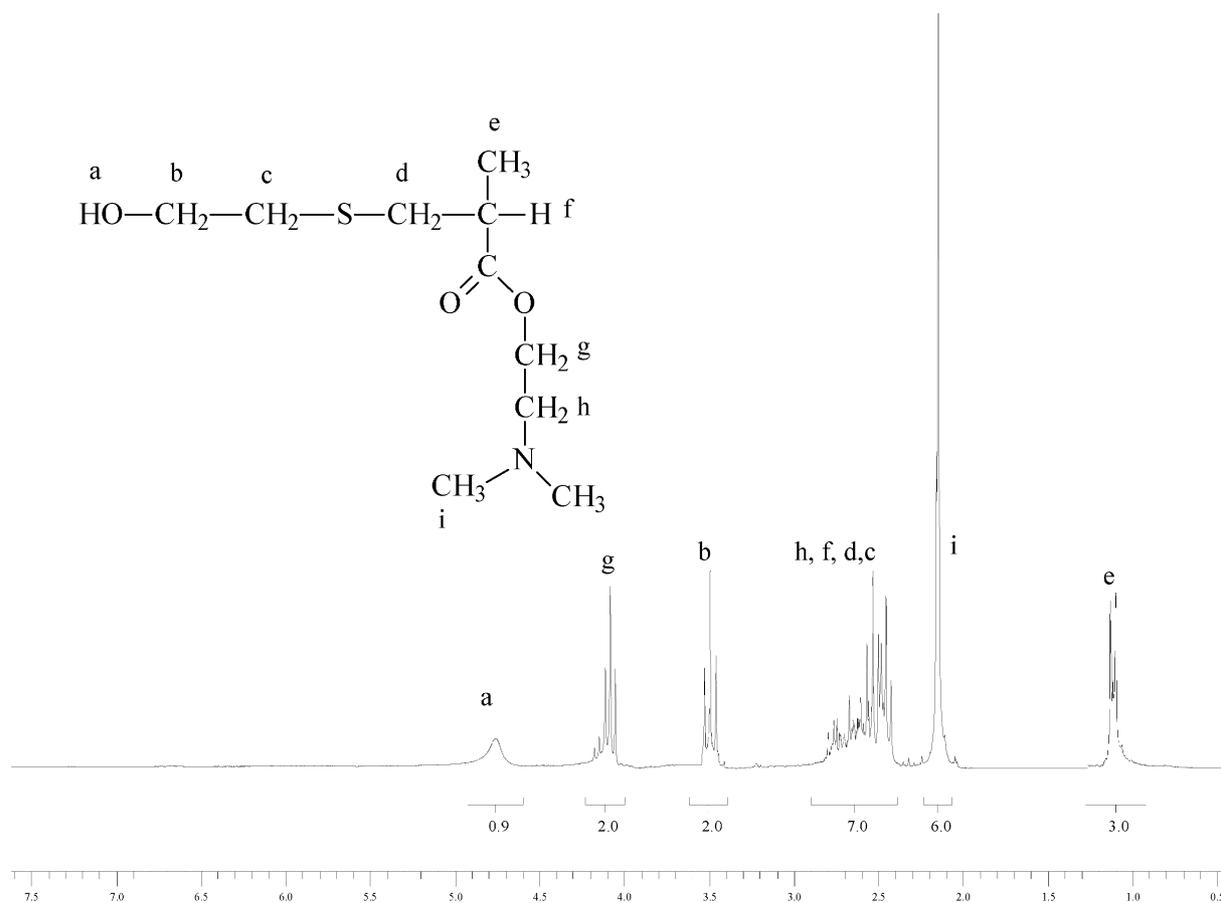


Fig. 2. ^1H NMR spectrum of the monoadduct (in deuteriated DMSO).

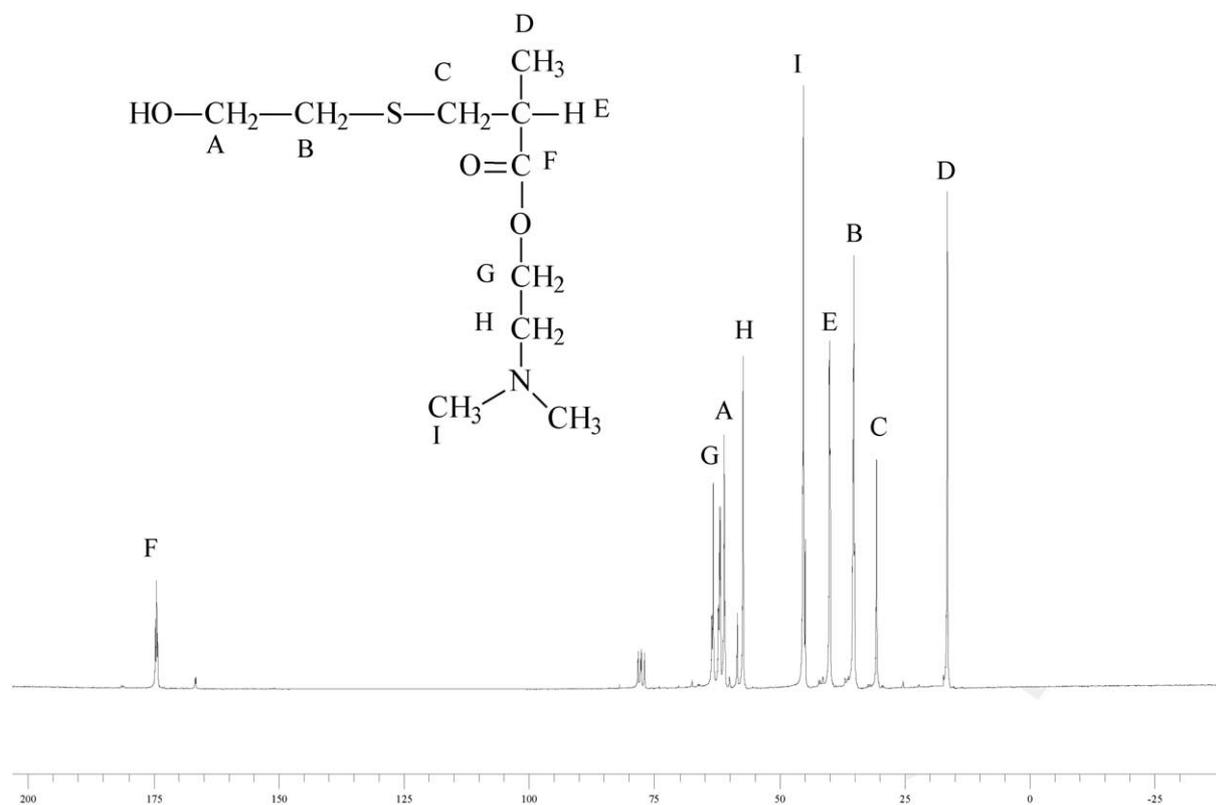


Fig. 3. ^{13}C NMR spectrum of the telomers (in CDCl_3 deuterium).

a mixture of polymer and monoadduct. Chromatogram of SEC (Fig. 1(a) and (b)) showed two peaks: the first one corresponding to high molecular weights (10,000 g/mol) and the second one corresponding to low molecular weights (235 g/mol). The separation of the compounds was achieved by precipitation in hexane (the monoadduct being soluble in hexane). ^1H NMR analysis showed that the product with low molecular weight (235 g/mol) could be the monoadduct. (Fig. 2). No peak was observed at 1.5 ppm (S–H group), 5.9 and 5.4 ppm (methacrylic protons). The alcohol function was observed around 4.8 ppm in DMSO (that was confirmed by a chemical shift when adding trifluoroacetic acid). The other peaks observed are: CH_2 (b) in α position to the alcohol function at 3.5 ppm (triplet), CH_2 (c) near the sulfur atom around 2.5 ppm, protons (d and f) coming from the double bond at 2.6 ppm, CH_2 (g) in α position of the ester group at 4.0 ppm, CH_2 (h) in α position to the nitrogen atom at 2.3 ppm and finally, methyl group (i) in α position to the nitrogen at 2.10 ppm. The integrals confirmed the structure of the monoadduct. The monoadduct was also confirmed by ^{13}C NMR (Fig. 3). The $\text{CH}_2=$ (128 ppm) and the signal $\text{C}(\text{CH}_3)=$ (136 ppm) signals have disappeared. The carbon $\text{CH}_2\text{--S}$ (B) and S--CH_2 (C) proved the structure of the monoadduct. The elemental analysis confirmed also this structure (experimental values: C 51.1%, H 9.1%, N 6.1%, O 20.40%, S 13.3%; theoretical values: C 51.04%, H 8.99%, N 5.95%,

O 20.40%, S 13.62%). The second peak of the chromatogram corresponding to high molecular weights (10,000 g/mol) was analysed by ^1H NMR. This peak corresponds to a poly(DMAEMA). Indeed, the peaks of CH_2 in α position to alcohol and the alcohol function do not appear at 3.5 and 4.8 ppm, respectively. This observation confirmed that the second peak corresponded to polyDMAEMA and not to telomers. Thus, in water, we obtained a mixture of monoadduct and polymer.

- In acetonitrile, it is necessary also to note the presence of an abnormal great amount of monoadduct, which explains the high value of the I_P (Fig. 1(c)). Thus, we have a mixture of monoadduct and telomer. It is possible to separate the monoadduct and the telomer (superior adducts) by precipitation in hexane. The structure of telomer was confirmed by ^1H NMR (Fig. 4). The presence of telogen could be observed by the proton signal CH_2 (b), which appears at 3.5 ppm and that of CH_2 (c) at 2.6 ppm. The DMAEMA signals appear at 4.0 ppm (CH_2 (g) in α position of the ester group), at 1.0 ppm, (assigned to CH_3 (e' and e)) and at 2.1 ppm, (attributed to CH_3 (i) in α position of nitrogen atom).
- In benzene, the chromatogram corresponds to a distribution known as 'telomer distribution', (Fig. 1(d)).

These results can be explained by a high C_T value when the telomerization solvent used is water or a water:acetonitrile mixture. When carrying out the titration of

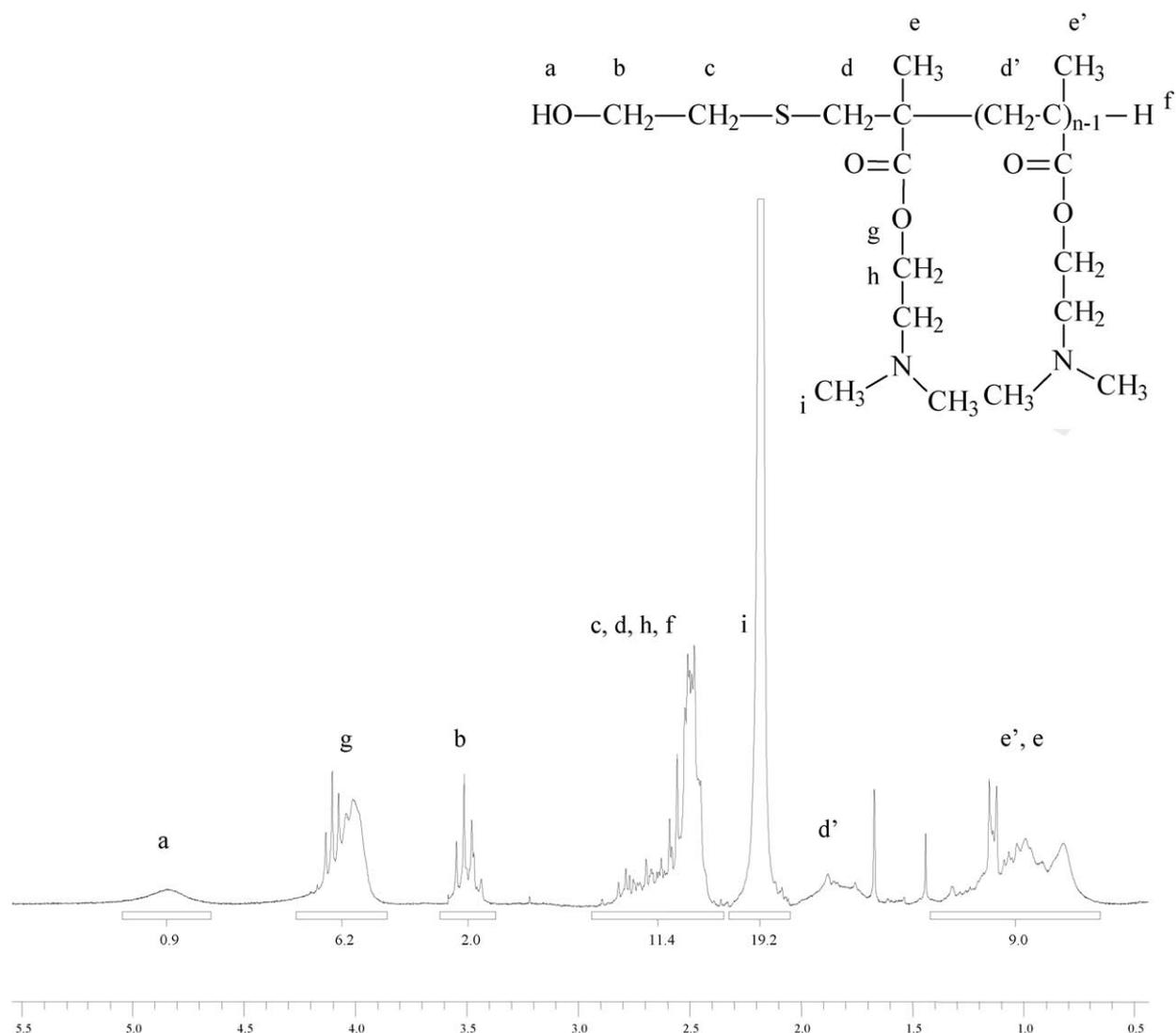


Fig. 4. ^1H NMR spectrum of the telomers (in DMSO deuterium).

thiols with iodine for low conversion rates of monomer, we observed the disappearance of more than 90% of thiol. To explain this result, it should be reminded that thiols are weak acids, with a pK_a close to 9.5 whereas DMAEMA bears a tertiary amine, with a pK_a value close to 11 [34]. Thus, an acido-basic equilibrium can occur between the tertiary amine and the thiol (Scheme 2).

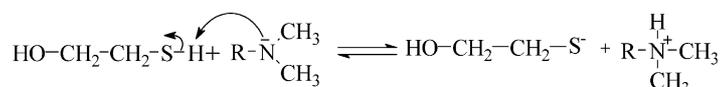
The concentration in monomer is in great excess compared to thiol concentration, so that this equilibrium can be shifted towards ionic species where the thiolate S^- presents a strong nucleophilic character. For example, Taylor et al. [35,36] studied the nucleophilic substitution of chlorotrifluoroethylene by thiolate and showed that this reaction is quantitative. Methacrylates and acrylates can

react with the nucleophilic compounds, such as primary amines (Michael reaction) or thiolate, (Scheme 3). This mechanism was enlightened in a previous work [20].

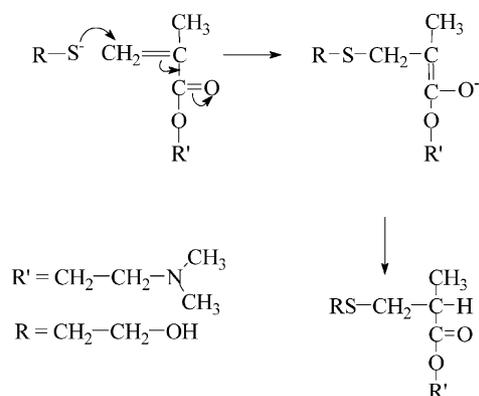
In acetonitrile/water mixture, (Table 4), we note that the molecular weight of the polymer fraction is constant whatever is R_0 . Under these conditions, the telogen does not affect the polymer length.

In the case of organic solvents, the acid–base equilibrium is different. Indeed, acetonitrile and benzene are not protic solvents, i.e. they are not proton donors. The stability of the ions in organic solvent is more reduced than that in the presence of water, this implies a different dissociation constant in organic solvents.

In benzene, the thiolate ions are slightly stabilized and



Scheme 2. Acid–base equilibrium between the mercaptoethanol and DMAEMA in water.



Scheme 3. Nucleophilic addition of thiolate to DMAEMA in aqueous medium (Michael Reaction).

the equilibrium is shifted towards the left (Scheme 2). So, the telomerization is carried out in normal conditions and nucleophilic addition is weak.

3.2. Determination of the transfer constant (C_T) in organic medium

In the case of telomerization, we have to consider three cases:

$C_T \ll 1$. The telogen has to be used as solvent or co-solvent to compensate the weak transfer constant. It is the case with methanol, chloroform [26].

$C_T = 1$. A good control of the molecular weight and polydispersity index I_p can be reached.

$C_T \gg 1$. Its interest to regulate the polymer length is very weak [37] and a mixture of polymers and monoadduct is obtained.

The C_T value has a great influence on the molecular weight but more especially on the I_p . Indeed, a C_T value higher than 1 involves a significant consumption of telogen at the beginning of the reaction.

In this study, C_T values were determined according to two methods and in two different solvents: benzene and acetonitrile. Water was not used because of the two concomitant reactions: telomerization and nucleophilic addition.

There are several methods permitting to determine the transfer constants. The first one and the most widely used was described by Mayo [38]. This method requires a plot of the inverse of the $(\overline{DP}_n)_i$ versus R_0 . This method comes from

Table 4
Influence of R_0 on \overline{M}_n for telomerization of DMAEMA with mercaptoethanol in a acetonitrile/water mixture (75/25 vol%)

R_0	\overline{M}_n (g/mol)
0	15,100
0.20	14,900
0.10	14,800

\overline{M}_n has been determined by SEC taking into account only the peaks attributed to telomers.

the general equation of Mayo which gives the degree of polymerization as a function of the transfer constants.

$$\frac{1}{(\overline{DP}_n)_i} = \frac{1}{(\overline{DP}_n)_0} + C_s \frac{[S]}{[M]} + C_I \frac{[I]}{[M]} + C_M + C_T \frac{[T]}{[M]} \quad (4)$$

with C_I transfer constant to initiator. C_s transfer constant to solvent. C_M transfer constant to monomer. C_T transfer constant to thiol. $(\overline{DP}_n)_0$ average polymerization degree calculated without transfer. $(\overline{DP}_n)_i$ average initial polymerization degree.

In our case, the transfer to telogens is higher than the other transfers, so Eq. (4) can be simplified to Eq. (5):

$$\frac{1}{(\overline{DP}_n)_i} = C_T \frac{[T]_0}{[M]_0} = C_T R_0 \quad (5)$$

The main drawback of this method is that it is only applicable for low conversion rates. The concentrations have to be constant so that, the difference between \overline{DP}_n (measured by SEC analysis) and $(\overline{DP}_n)_i$ would be weak.

The method of O' Brien and Gornick [39] allows to measure C_T taking into account the conversion rates:

$$\text{Ln} \frac{[T]_t}{[T]_0} = C_T \text{Ln} \frac{[M]_0}{[M]_t} \quad (6)$$

Thus, plotting $\text{Ln}([T]_t/[T]_0)$ versus $\text{Ln}([M]_t/[M]_0)$ permits to calculate C_T value from the slope of the obtained straight line.

The telomerization of DMAEMA has been studied using the two methods cited above, at 70 °C, in the presence of AIBN and in two different solvents: acetonitrile and benzene. Each reaction was monitored by sampling, and each aliquot was quenched in ice to stop the reaction. The monomer and telogen conversions were determined, respectively, by GC and iodine titration.

3.3. Determination of C_T by Mayo's method

In these experiments, polymerizations were carried out with a constant concentration of AIBN while the thiol-monomer ratio (R_0) was varied.

The polymerization average number degrees were

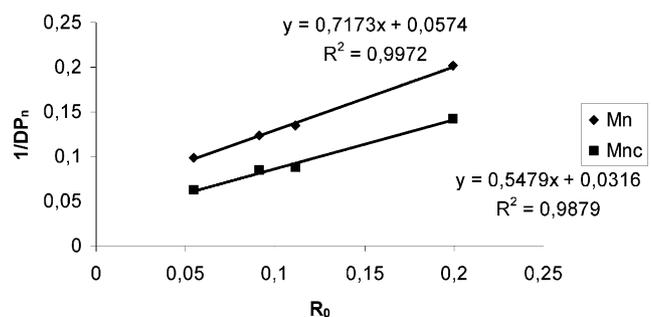


Fig. 5. Evaluation of the transfer constant of DMAEMA with 2-mercaptoethanol at 70 °C in acetonitrile.

Table 5
Variation of the transfer constant versus solvent nature

Solvent	C_T^* (Mayo)	C_T (Mayo)
Benzene	0.54	0.57
Acetonitrile	0.53	0.72

C_T^* = transfer constant calculated taking into account only the peaks of telomers distribution (SEC). C_T = transfer constant calculated taking into account both peaks of telomers and monoadduct.

measured by SEC analysis and \bar{DP}_n was calculated taking into account the presence of monoadduct \bar{M}_n , or after correction by subtracting the peak coming from the monoadduct. As predicted by Mayo's equation, linear plots are observed (Fig. 5).

In Table 5 are listed the C_T values given by the slope of $1/\bar{DP}_n$ versus R_0 .

In benzene, the variation is relatively weak between C_T^* and C_T . On the other hand, the C_T values are very different in acetonitrile, proving a higher consumption of thiol by nucleophilic addition. When comparing C_T^* values calculated only on the telomer distribution, we note that the values in benzene and acetonitrile are quite similar. These C_T values correspond to the values usually observed for the mercaptoethanol with methacrylates [40,41].

3.4. Determination C_T by O'Brien's method [41]

In these experiments, polymerizations were carried out in the same conditions as previously described.

Fig. 6 summarizes the results of telomerization in benzene with $R_0=0.20$. Conversion yield of telogen was obtained by a titration with iodine solution and that of monomer by GC. This figure shows the linear relationship between $\ln([T]_0/[T]_t)$ and $\ln([M]_0/[M]_t)$ for each solvent, and the slopes give C_T values of 1.29 in acetonitrile and of 0.71 in benzene.

We observe that the values of the transfer constants determined by Mayo and O' Brien are not in agreement. This difference comes from the method of calculation of C_T . In Mayo's method, C_T is calculated on the basis of the measured molecular weights whereas O' Brien's method involves the thiol consumption including the consumption by nucleophilic addition and telomerization reaction. Thus, O' Brien's method is more sensitive to the secondary reaction than that Mayo's method.

Table 6
Evolution of molecular weights and I_p as a function of R_0

R_0	\bar{DP}_n^f	\bar{M}_n (g mol ⁻¹)	\bar{DP}_n^{SEC}	I_p	\bar{DP}_n^{NMR}
0.66	1.5	300	1.4	1.5	1.3
0.3	3.33	650	3.6	1.6	3.2
0.25	4	750	4.3	1.6	4.0
0.20	5	900	5.2	1.7	5.10
0.125	8	1400	8.40	1.8	8.5

\bar{M}_n = molecular weight measured by SEC analysis. \bar{DP}_n^{SEC} calculated by Eq. (1). \bar{DP}_n^f is calculated by Eq. (3).

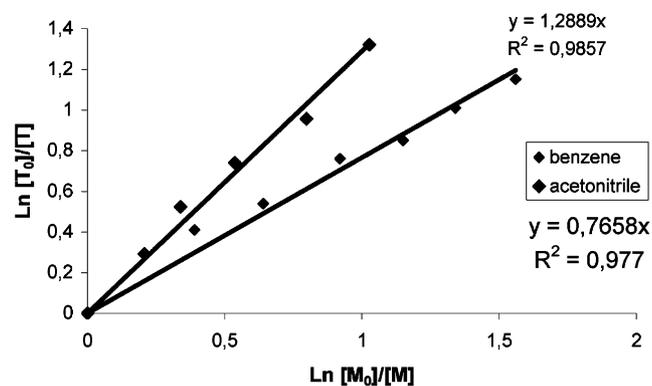


Fig. 6. Evaluation of the C_T constants according to O'Brien's method for free radical telomerization of DMAEMA with mercaptoethanol in different solvents.

3.5. Influence of the nature of the solvent on the $k_p/\sqrt{k_{te}}$ value

In radical polymerization, the overall rate constant of polymerization depends on the kinetic constant $K = k_p/\sqrt{k_{te}}$.

With k_{te} is the termination rate constant, k_p is propagation constant.

Thus, the constant K is linked to the various kinetical constants and to concentrations by the following relation:

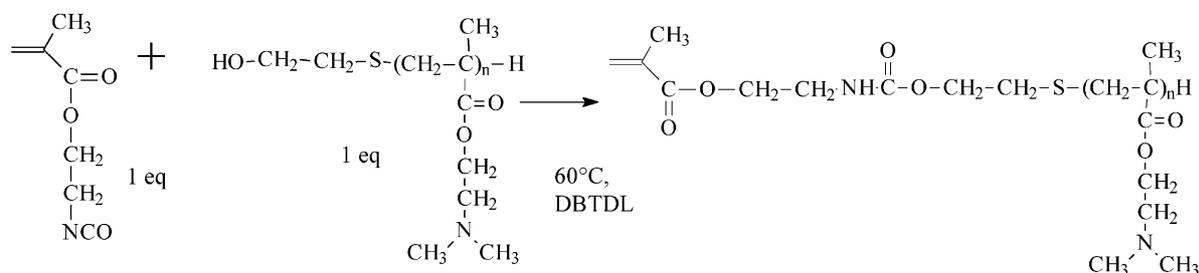
$$v_p = \frac{k_p}{\sqrt{k_{te}}} \sqrt{fk_d} \sqrt{[I_2]} [M] \quad (7)$$

with k_d : initiator decomposition rate constant, f : efficiency factor for the conversion of initiator to active radicals (initiator efficiency), $[M]$, and $[I_2]$ are, respectively, the instantaneous concentration in monomer and initiator.

Tobolsky [42] integrated Eq. (7) to Eq. (8).

$$\ln \frac{[M]_0}{[M]} = 2 \frac{k_p}{\sqrt{k_{te}}} \sqrt{\frac{f}{k_d}} \sqrt{[I_2]} (1 - \exp(-k_d t/2)) \quad (8)$$

Thus, plotting $\ln([M]_0/[M]_t)$ versus $(1 - \exp(-k_d t/2))$ permits to calculate $k_p/\sqrt{k_{te}}$ from the slope of the obtained line. The decomposition constant of AIBN is independent of the solvent nature [43]. In our case, $k_p/\sqrt{k_{te}}$ equals to $0.257 \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$ in acetonitrile and $0.285 \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$ in benzene that is not very dependent with the nature of solvent.



Scheme 4. Synthesis of macromonomers from telomers of DMAEMA.

3.6. Synthesis of macromonomer with the isocyanatoethyl methacrylate (IEM)

Telomers are good precursors of the synthesis of macromonomers by conversion of the terminal function coming from the telogen into unsaturation (Scheme 4).

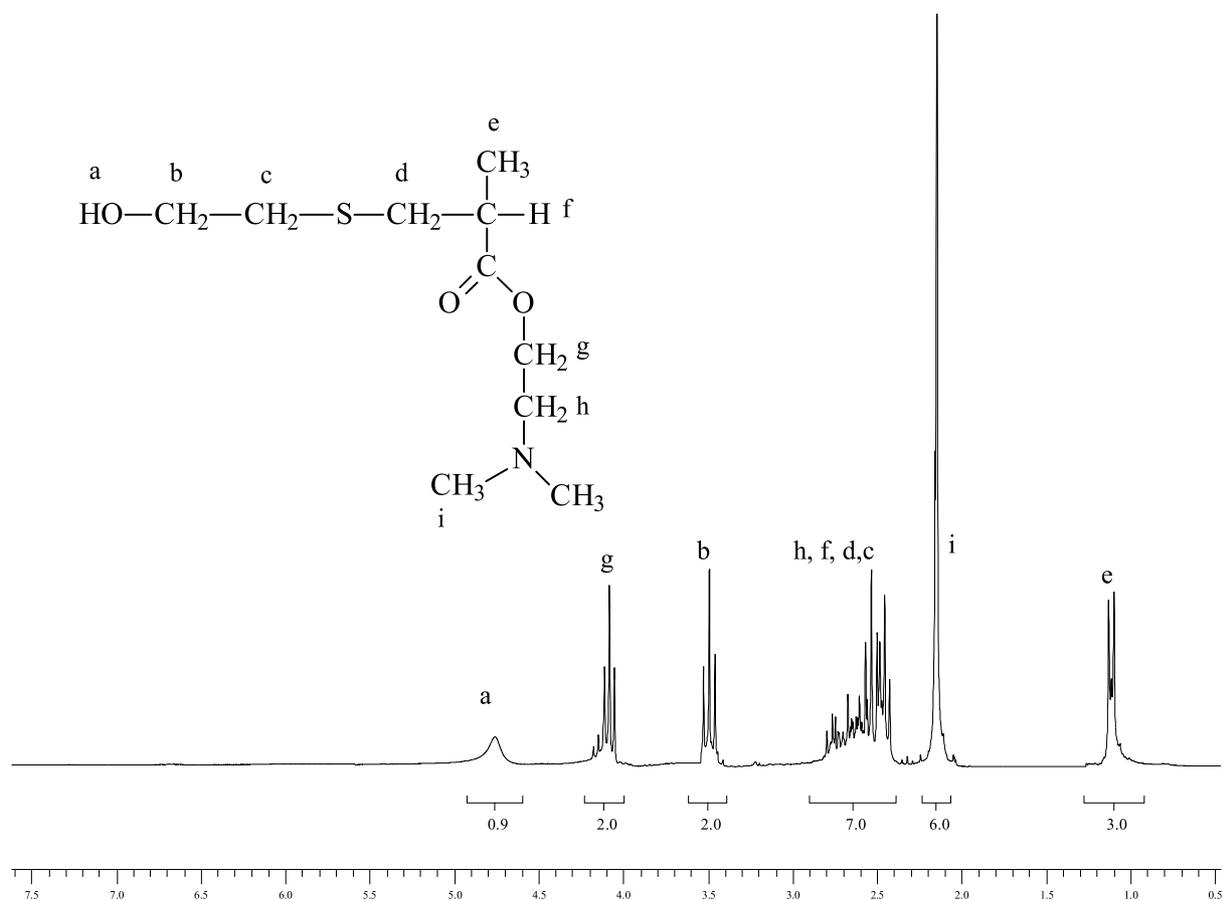
At first, we synthesized a model compound to make easy the interpretation of ^1H NMR spectra. Thus, the monoadduct of mercaptoethanol with DMAEMA was obtained by stoichiometric addition of the two reagents at 80°C in acetonitrile without initiator, as described in a previous work [20]. The structure was confirmed by ^1H NMR (Fig. 2). No peak was found at 1,5 ppm (S–H group) and 5.9 and

5.4 ppm (methacrylic protons). SEC analysis showed no residual peak from mercaptoethanol and DMAEMA and the appearance of a unique peak. The polydispersity index was 1.05 meaning a well-controlled reaction.

In a second step, telomerization of DMAEMA with mercaptoethanol was achieved using AIBN as initiator in benzene at 70°C . This solvent was used due to its low transfer constant and since the nucleophilic addition was weak in these conditions as demonstrated before.

We synthesized different telomers varying R_0 (Table 6) and samples were analysed by SEC and NMR.

The determination of the \overline{DP}_n using ^1H NMR (Fig. 4), was achieved through the integration of the peaks located at

Fig. 7. ^1H NMR spectrum of the monoadduct after reaction with IEM (in deuteriated DMSO).

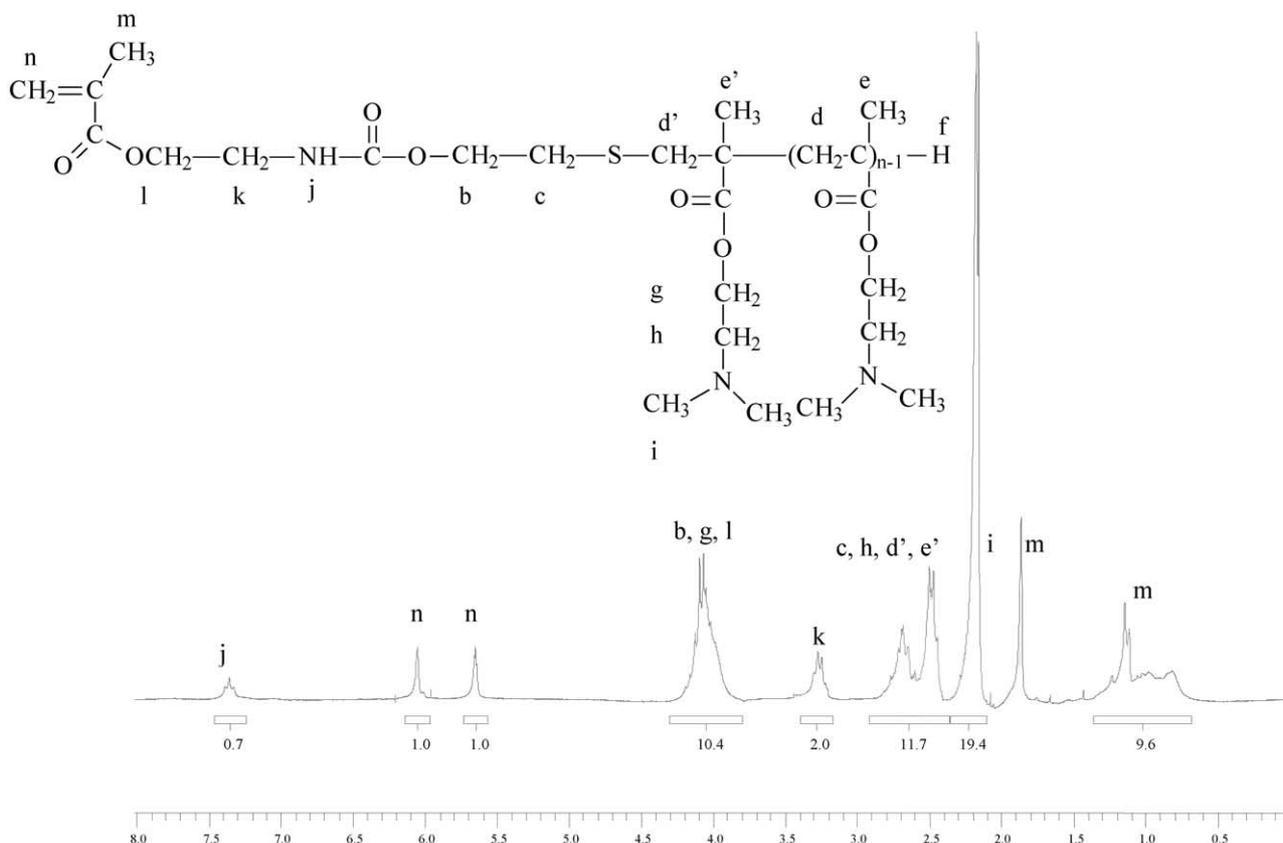


Fig. 8. ^1H NMR spectrum of the telomers after reaction with IEM (in DMSO deuterium).

4 ppm (CH_2 in α position of the ester group) and at 3.5 ppm (attributed to CH_2 in α position of the alcohol function).

$$\text{DP}_n^{\text{NMR}} = \frac{\int \text{CH}_2(\text{at } 4.0 \text{ ppm})}{\int \text{CH}_2(\text{at } 3.50 \text{ ppm})} \quad (9)$$

Results obtained by NMR and SEC analysis are in good agreement (Table 6), what confirms that nucleophilic reaction is negligible in benzene.

The macromonomers were synthesized by reaction of an isocyanate bearing a methacrylate type unsaturation (Scheme 4). This reaction was catalyzed by dibutyl tin dilaurate (DBTDL). For the first attempts of functionalization, we observed the appearance of a peak around 6.1 ppm. To characterize this peak, we achieved the synthesis of urea while introducing IEM with water. The spectra of the product obtained showed a peak at 6.1 ppm (attributed to NH of urea). Thus, addition of IEM to the telomers needs to operate in a dried medium. The kinetics of the reaction was determined by measuring the decrease of the isocyanate peaks at 2250 cm^{-1} and that of alcohol at 3400 cm^{-1} .

The ^1H NMR analysis showed the disappearance of the OH group peak (at 4.8 ppm) (Figs. 2 and 7) and an increase of the peak at 4.0 ppm. Furthermore, the peak located previously at 3.5 ppm which was ascribed to the CH_2 group in α position of a alcohol function, was now observed at

4 ppm, characteristic of a CH_2 in α position of the urethane group. The CH_2 in α position of the isocyanate function was downfield from 3.6 to 3.3 ppm and the CH_3 of IEM shifted from 1.9 to 1.8 ppm, what confirms the disappearance of the isocyanate function. At last, a peak around 7.4 ppm characteristic of the NH of urethane group was observed (Figs. 6 and 7), but this integral is not quantified.

SEC analysis confirmed that the reaction was total since the peak of monoadduct was shifted from 235 to 390 g/mol.

Oligomers described in Table 6 were functionalized according to the same procedure. The reaction was monitored by FT-IR, where the isocyanate band (2250 cm^{-1}) totally disappeared after 6 h at 60°C . The complete reaction was confirmed by ^1H NMR analysis (Fig. 8) where the CH_2 in α position of the OH group at 3.5 ppm disappeared, and the peak at 4 ppm increased as observed in the case of the monoadduct. The protons of the methacrylic function remained unchanged meaning that no polymerization occurred. The SEC analysis confirmed the increase in molecular weight without any changes in I_p value.

3.7. Copolymerization of macromonomer with styrene

In a last part, we studied the copolymerization of our macromonomer with styrene and so, verified its reactivity. Copolymerization was carried out in acetonitrile at 70°C

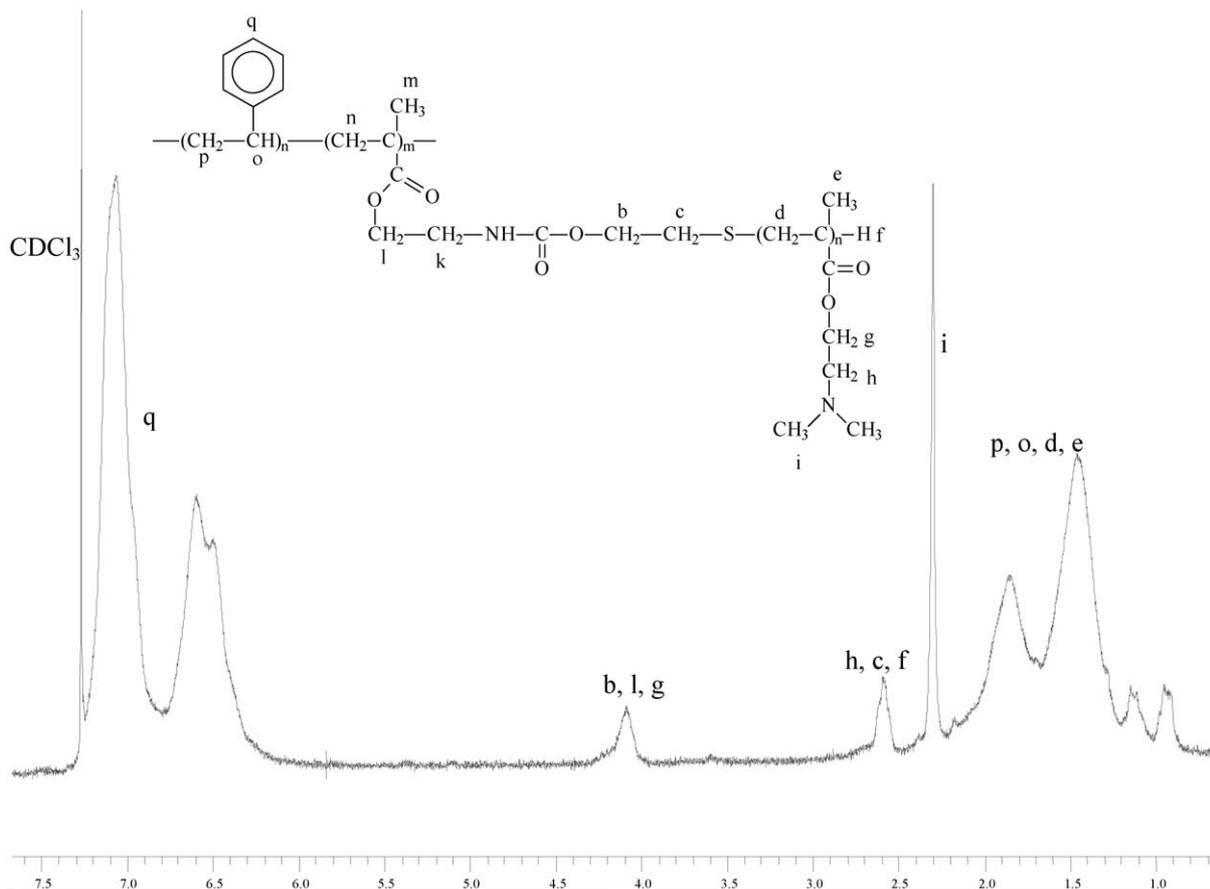


Fig. 9. ^1H NMR spectrum of the copolymer styrene/macromonomer in CDCl_3 .

and with AIBN. The concentrations of styrene and macromonomer were, respectively, adjusted at 1 mol/l and 0.1 mol/l. Thus, the copolymers obtained were precipitated in water to eliminate non reacted macromonomer (this last being soluble in water). ^1H NMR spectrum in CDCl_3 confirms the insertion of the macromonomer within the copolymer by the various signals located at 4.00, 2.60 and 2.30 ppm and by the disappearance of the signal at 5.6 and 6.1 ppm these last being attributed to the double bond (Fig. 9). The CH_2 signals of macromonomer in α position of ester groups (b,l,g) appeared at 4.00 ppm, the CH_3 (i) signal of macromonomer in α position of amine group was observed at 2.3 ppm and the CH_2 (h) group in α position of amine group at 2.5 ppm. The styrenic protons

appeared around 6.5–7.0 ppm (aromatic group) and 1.5–2.0 ppm ($\text{CH}_2\text{-CH}$).

FT-IR analysis confirmed the presence of ester groups in the copolymer (C=O at 1730 cm^{-1}) and that of aromatic group (3050 cm^{-1}).

We calculated the molar ratio (W_1) of the macromonomer with respect to styrene in the copolymer (after precipitation) using Eq. (10):

$$W_1 = \frac{\int g + b + l/2n + 4}{\int q} \quad (10)$$

Where

$$\int g + b + l \Leftrightarrow 2 + 2 + 2\text{DP}_n \Leftrightarrow 4 + 2n \quad (11)$$

Table 7

Experimental conditions for the copolymerization of the macromonomer (macro.) with styrene

Copolymers	Initial styrene content (mol)	\bar{M}_n macro. g mol^{-1} *	Initial macro. content (mol)	Molar ratio of styrene in the copolymer (W_1)	Molar ratio of macro. in the copolymer (W_2)	\bar{M}_n g mol^{-1} *
1	0.1	430	0.01	0.90	0.10	12,800
2	0.1	850	0.01	0.91	0.09	16,400
3	0.1	1150	0.01	0.91	0.09	19,000

* \bar{M}_n determined by SEC analysis with polystyrene standards.

This equation is based on the signal at 4.00 ppm attributed to three types of CH₂ (b,l,g) and that of aromatic protons. Value n stands for the \overline{DP}_n of the macromonomer.

Table 7 summarizes the results obtained with the different synthesized copolymers.

This table shows the good reactivity of the macromonomer meaning that this last can be used in copolymerization to obtain new graft copolymers.

4. Conclusion

The kinetics of the telomerization of DMAEMA with mercaptoethanol shows that, in a protic solvent, the competition between the telomerization and the nucleophilic addition induces an increase of the polydispersity index due to an abnormal quantity of monoadduct and formation of non functionalized polymer. In these conditions, it is impossible to synthesize telomers. However, using non protic solvents like benzene or acetonitrile decreases the nucleophilic addition and allows to synthesize well-defined telomers. The transfer constant of mercaptoethanol to DMAEMA was determined by two methods: O'Brien's method ($C_T=1.28$ in acetonitrile and $C_T=0.70$ in benzene) and Mayo's method ($C_T=0.63$ in benzene, $C_T=0.72$ in acetonitrile). These differences observed in the two different solvents can be explained by the nucleophilic addition of the thiol to monomer. Furthermore, the ratio $k_p/\sqrt{k_{te}}$ is not very dependent on the nature of the solvent: $0.257\text{ l}^{1/2}\text{ mol}^{-1/2}\text{ s}^{-1/2}$ (acetonitrile) and $0.285\text{ l}^{1/2}\text{ mol}^{-1/2}\text{ s}^{-1/2}$, (benzene)

At last, these oligomers were functionalized with 2-isocyanatoethyl methacrylate to obtain macromonomers. These macromonomers were efficiently copolymerized with styrene to obtain new graft copolymers.

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