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SYNTHESIS OF END-FUNCTIONALIZED OLIGOMERS BY ONE-BATCH CATIONIC POLYMERIZATION.

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Summary

The synthesis of end-functionalized oligomers by cationic polymerization is examined. Special attention is devoted to the problem of achieving this synthesis in a one-batch process, starting from the monomer and an additive which is properly functionalized. The functions of interest are chosen among the pseudohalide functions, azide and isothiocyanate. The functionalizing cationic polymerization of 2-methylpropene was the main system discussed in this context. A brief mention about the behavior of 1,3-pentadiene, isobutylvinylether, and 2-methyl-2-oxazoline is presented. It is shown that depending upon the strength of the Lewis acid and the experimental conditions, the specificity of the functionalization and the possibility of a controlled polymerization can be obtained. The experimental observations can be rationalized by assuming an equilibrium between the active species and the dormant chain ends containing a halide or a pseudohalide. This assumption allows to explain the synthesis of polymers containing two different types of chain termini but corresponding to a narrow molecular weight distribution.

I- Introduction

Our laboratory has been involved in the functionalization of oligomers by cationic polymerization for a long time. More precisely, the goal was a direct functionalization by polymerization from the monomer in a one batch process. Not only, a good control of molecular weight and polydispersity index was looked for, but also the functionalization by a desired chain end such as a pseudohalide was aimed. Among these functions the azide and the isothiocyanate were the more thoroughly investigated, because they were assumed to be sufficiently inert to the conditions of the ordinary cationic polymerization. It will be seen below that this assumption is not always verified. It was expected that, since it was obvious from the work of Kennedy's group that oligomers terminated by a tertiary chloride are obtained in a one-step process starting from a mixture of 2-methylpropene and a benzylic chloride, oligomers could be similarly obtained starting from a mixture of monomer and an initiator suitably functionalized by a pseudohalide function. These functions are interesting because they offer the way to further chemistry such as cycloaddition or transformation into primary amine function for the azide group (1), or addition for the isothiocyanate function (2). It has been published that organic pseudohalides can react with carbenium ions. This reaction in the case of the azide group is known as the Schmidt reaction of the synthesis of the iminium ions (3):

$$\text{R-C}^+\text{,A}^- + \text{R'-C-N}_3 \longrightarrow [\text{R-C-NR'=C}]^+\text{,A}^- + \text{N}_2$$

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As a consequence of this reaction, the possibility of obtaining the desired functionalization can be questionned. Some work will be described below to clear up this point.

The direct functionalization can be achieved by two ways, either by initiation from a functionalized initiator, or by exchange reaction during polymerization. The first one can be summarized as follows:

$$\text{R-X} + \text{pM} \xrightarrow{\text{MX'n}} \text{R-(-M-)}_{\text{p}}\text{-X}$$

where R-X is a functionalized initiator and M is the monomer. X is a halide or a pseudohalide function. MX'_n is a suitable Lewis acid. The second type of synthesis is represented by the following equation:

$$\text{R-(-M-)}_{\text{p-1}}\text{-M}^{+}\text{,C}^{-} + \text{A-X} \longrightarrow \text{R-(-M-)}_{\text{p}}\text{-X} + \text{A-C}$$

where A-X is a molecule susceptible to exchange its X function with the Lewis acid to give the counteranion of the active species, or with the active species itself. In this study, the A-X molecule was trimethylsilylazide (TMSA) which was purposedly added to a cationically polymerizing system in order to obtain the desired exchange. It can be questionned to know whether the first system above can also be a simple exchange, the R-X molecule being simply a source of -X function. The work described here was also aiming at answering this question, and at determining what would be the easiest way to achieve the desired synthesis.

II- Results and discussion

An important part of the work which is going to be described below was effected with azide group and to a lesser extent with isothiocyanate function. The reason for such choice is that the reactivity of these two pseudohalide functions is sufficently low to be used in similar conditions as the halides. However, to ascertain this point, a preliminary work was carried out to determine at which conditions the cationic polymerization of various monomers could be obtained in the presence of azide function. It was shown that when polymerizing the usual olefins such as 2-methylpropene and styrene the initial concentration of azide function is to be kept lower than that of the Lewis acid (4). The reason for such a condition is to be found in the complexation of the azide function by the Lewis acid which prevents its further reaction with the active species of the cationic polymerization. This is the reason why an excess of free pseudohalide must be avoided, and why with these monomers most of the work was effected in conditions of pseudohalide concentration lower or equal to that of the Lewis acid. In the case of vinyl ethers such as isobutyl vinyl ether, it will be seen below that the condition on the concentration of azide groups is less strict. For instance, the cationic polymerization of isobutylvinylether initiated in the presence of stanic chloride does not seem to be prevented by the presence of an excess of TMSA. It is clear that qualitatively, the reaction of the pseudohalide function with the active species must be a function of the acidity of the active species, and that of the vinylethers is less strong than that of the olefins. Similarly, with heterocyclic monomers, it will be seen below on one example that the cationic polymerization can be carried out in the presence of a large excess of TMSA.

In the various situations encountered in this study, different results were obtained. It is an object of this paper to discuss the results of experiments aiming at the production of functionalized oligomers, in a one-batch process, according to the values measured for the polydispersity index, either a polydispersity index equal or higher than 2, or with a polydispersity index lower than 2. New and old works are presented in order to allow to draw conclusions on the functionalization mechanism.

II-1- Functionalizing cationic polymerization with a polydispersity index equal to two or higher.

A first example which must be described here for the sake of completeness is the polymerization of 2-methylpropene initiated by 1-azido-1methylethylbenzene, also called cumylazide, in the presence of BCl_3 in CH_2Cl_2 at -50°C. Some representative results are shown on Table 1.

Table 1

Polymerization of the system 2-methylpropene (IB)/Cumyl-azide(Cum-N_3)/BCl_3/CH_2Cl_2, at -50°C, [BCl_3] = $1.6.10^{-2}$M, 30 min.

N°	[IB] M	Cum-N_3 M	Yield %	Mn D	f_{φ}*	f_{N3}**
1	1.1	10^{-2}	30	1600	1.1	0
2	1.1	$1.5.10^{-2}$	80	1700	1.1	0

* Aromatic nuclei content, by NMR spectroscopy and SEC.

**Azide group content, by IR spectroscopy and SEC.

It must be mentionned before the interpretation of these results that initiation takes place from the cumyl azide initiator (φ-$C(CH_3)_2$-N_3) since without it initiation was not observed in these conditions, and that not only the yield was increasing with the initiator concentration but that all macromolecules contain an aromatic nucleus as shown by the aromatic molar content which is close to one (5). However, the infrared analysis showed that the polymer did not contain any measurable amount of azide group. We conclude from these observations that in our case the following reaction did not take place:

$$PIB^{+}, BCl_3N_3^{-} \longrightarrow PIB\text{-}N_3 + BCl_3$$

In other words, the complex counteranion $BCl_3N_3^-$ do not release the azide moiety. NMR spectroscopy showed that these polymers contained terminal chloride. Obviously, the interaction between BCl_3 and Cl^- is less strong than with N_3^-. The incorporation of the chloride ion is a termination reaction and explains the yields which were not complete. This first example tells that the functionalization efficiency by the pseudohalide group is governed by the properties of the counteranion in which the pseudohalide anion is incorporated. In this system, the molecular weight distribution does not exhibit any narrowing tendancy which demonstrates that termination and transfer occur at random.

A second example is provided by the polymerization of 1,3-pentadiene in the presence of TMSA initiated by $AlCl_3$ in a non polar medium. In this system it was shown that direct initiation is responsible for the active species production (6). Some characteristics of this system are described in Table 2.

Table 2

Polymerization of the system 1,3-pentadiene ([2.3M])/TMSA/$AlCl_3$ ($[AlCl_3] = 2.3.10^{-2}M$)/hexane, at room temperature, reaction time = 2 h.

N°	$\frac{[TMSA]}{[AlCl_3]}$	Yield %	Mn soluble fra. D	I* soluble fra.
1	0	93	7000	35
2	1	26	1000	25
3	4	9	600	5

*Polydispersity index.

The first observation is that the presence of TMSA strongly reduced the yield. As expected, a large excess of TMSA was very detrimental (run 3). Analysis of the polymers shows that the polymers produced in the presence of TMSA contained chloride and a small amount of azide groups. To this respect, a comparison of this phenomenology using $AlCl_3$ with an other work carried out on the same monomer in similar conditions but using $AlEt_2Cl$ is interesting (7). In this last work, it was shown that with this Lewis acid, initiation did not mainly proceed directly since in the absence of any initiator, the yield was low. It is interesting to notice that in the presence of TMSA no modification was reported in term of yield, molecular weight and polydispersity index. TMSA was inert, while in the presence of an other initiator such as cumyl chloride the polymerization was fast with high conversion and a high proportion of crosslinked product. The same paper (ref. 7) reports that in the presence of bis(azidomethylethyl)benzene (BAMEB), the yield is much better, producing a totally soluble polymer (7). It is clear that in this system, the acidity of the Lewis acid is high enough to induce polymerization from the initiator even in non polar solvent, while it is not able to give any exchange with TMSA. At last, it is important to note that polymerizations carried out in the presence of chlorinated initiators, such as cumyl chloride and $AlEt_2Cl$, produced a high proportion of insoluble material with a slightly better yield than without.

The results of 1,3-pentadiene polymerizations with $AlCl_3$ showed that functionalization constituted a termination reaction, as shown by the reduction of the yield, molecular weight and polydispersity index (Table 2). In agreement with this conclusion, it is worth noting that in the presence of TMSA and $AlCl_3$, the insoluble fraction was strongly reduced (8). A short study was carried out in our laboratory on the point to know whether the polymer could be functionalized by an azide group for the system based on aluminum trichloride. A poly(1,3-pentadiene) was synthesized in the presence of the system BAMEB-$AlCl_3$, and analysed by infrared and ^1H NMR spectroscopies (8). It was shown that, after careful cleaning, the polymer contained a small amount of azide group, but no aromatic nucleus. This result is interpreted as showing that azide group functionalization results from an exchange reaction, and not from initiation or transfer from BAMEB. In that case, BAMEB behaves as a simple source of azide groups like TMSA. This conclusion could seem contradictory with the results reported in ref.7 showing initiation from BAMEB. It must be recalled that in the $AlCl_3$-based system initiation proceeds directly, producing by self ionization an ion pair on which the exchange can take place. It is unfortunate that not enough information was available on the characteristics of polymerizations carried out in the presence of $AlEtCl_2$, and this situation prevents to draw more conclusions from the comparison.

In the same context, the polymerization of isobutylvinylether initiated in the presence of TMSA and $SnCl_4$ in polar solvent must be reported (9). Some characteristic results are described in Table 3. In this system, in the absence of TMSA, initiation should be cocatalytic, using residual moisture. The polymerization yield was never complete, showing that some termination reaction occured. Whatsoever, the molecular weight did not appreciably change with TMSA concentration. This observation is difficult to explain taking into account that the oligomers were functionalized by an azide group when the TMSA concentration was high enough. Since the polydispersity index remained around 2, it must be accepted that the mechanism which governs the interruption of chain growth, functionalization, is predominant. Since. the molecular weight did not decrease when TMSA concentration increased, it can be suggested that functionalization is zero order in active species concentration which allows to suggest that the functionalization is due to the release of the azide group by the counteranion the chain ends. The primary reaction of TMSA must happen on the Lewis acid itself, and this is why nothing can be assumed on the initiation mechanism. It is also to be noted that a large excess of TMSA does not seem to be detrimental to the active species, since the best polymerization yield is obtained with the highest TMSA concentration. This is probably to be assigned to the fact that in the case of IBVE polymerization the active species are less acidic than in the case of olefins. This example tells that functionalization by a pseudohalide is possible but not with a complete yield, and that this functionalization does not allow a control of the molecular weight. However, this situation meets the requirement of being possible in a one-batch process.

Table 3

Polymerization of the system IBVE (0.7 M)/TMSA/$SnCl_4$ ($4.7.10^{-2}$)/CH_2Cl_2, 20°C, t = 20 min.

N°	[TMSA] M	Yield %	Mn_{SEC}* D	I**	f_{N3}
1	$1.4.10^{-2}$	70	1200	2.4	0.3
2	$4.1.10^{-2}$	70	1300	2.3	0.75
3	$6.2.10^{-2}$	67	1400	2.5	1.0
4	$10.3.10^{-2}$	83	1400	2.2	1.1

*In eq. P. St.

**Polydispersity index.

An other example of interest to be discussed in this context is represented by the polymerization of 2-methyl propene in a polar medium (CH_2Cl_2) at -70°C in the presence of BF_3 (5). A summary of the results is shown on Table 4. These results are dealing with two different initiators, the 2,4,4-trimethyl-2-azidopentane (H-TMP-N_3) and the 2-phenyl-2-azidopropane (cumylazide). It is interesting to note that the yields are complete when the azide concentration was not higher than the Lewis acid concentration. Run 3 shows that on the contrary, when the azide concentration was higher than that of BF_3, a decrease of the yield is observed. About initiation, the cocatalytic mechanism is likely (10). On the other hand, a coinitiation mechanism must be also observed, and this is witnessed by the bimodal distribution in the case of the polymer synthesized in the presence of H-TMP-N_3 (run 1). The fact that two different active species are at work in the case of run 1 entails that the functionalization is not the result of a simple transfer occuring on H-TMP-N_3.

In the case of initiation on cumylazide, the macromolecules are containing around one aromatic nuclei per chain. The chain ends in the case of run 2 contain at the same time azide groups and unsaturations. It must be concluded that two mechanisms of interruption of chain growth are at work at the same time, the functionalization by the azide group and transfer. These two competing mechanisms help to understand why the polydispersity index is higher than two. The question is to know whether the cocatalytic initiation can also be observed in the case of cumylazide initiation. The high phenyl ring content shows that at least transfer to cumylazide should be very important. Since the azide content is lower than the phenyl ring content, some dehydroazidation or transfer to monomer must occur. However, it must be noted that transfer to monomer is probably negligible because a high phenyl ring content is measured. The fact that the molecular weight is independent of the Lewis acid concentration is an argument in favour of initiation on cumyl azide and of the disappearance of the cocatalytic initiation. The explanation of this interesting characteristic of the use of azide group containing initiators is to be found in the competion between water molecules and cumylazide molecules for complexation by BF_3 molecules. It is clear that the reaction leading to carbocations is faster in the case of coinitiation with cumylazide than in the case of the sequence: cocatalyst reacts with the Lewis acid to give the so-called complex acid which in turn reacts with the monomer to give the carbocation. Several systems behave similarly as far as cocatalysis is concerned, and to this respect they are worth of attention due to the increase of selectivity they confer.

Table 4
Polymerization of the system 2-methylpropene (IB)/R-N_3 /BF_3/CH_2Cl_2, at -70°C, t = 50 min.

N°	IB M	R-N_3 M	BF_3 M	Yield %	Mn D	f_{φ}*	f_{N3}**
1	1.1	H-TMP-N_3 $4.8.10^{-2}$ ****	$4.8.10^{-2}$	100	2600***	-	0.45
2	1.1	Cum-N_3 $5.0.10^{-2}$ ****	$5.0.10^{-2}$	100	1300	0.8	0.5
3	1.1	Cum-N_3 $5.0.10^{-2}$	$1.5.10^{-2}$	80	1300	1	0.8

* Aromatic nuclei content, by NMR spectroscopy and Mn SEC (in eq. pSt).
**Azide group content, by IR spectroscopy and SEC.
***bimodal distribution.
****H-TMP-N_3 = tBu-CH_2-$C(CH_3)_2$-N_3, Cumylazide: φ-$C(CH_3)_2$-N_3

The results of run 3 (Table 4) could have been assigned to a predominant transfer to cumyl azide rather than to coinitiation on cumylazide, since the functionalization by aromatic nuclei and by azide group are close to each other. In order to determine the answer to this question, run 3 must be compared to run 2. This last experiment shows that when the Lewis acid concentration is increased, one loses on the side of functionalization. This is due not only to some transfer (unsaturated chain ends and protonic reinitiation on the other end), but also to deshydroazidation since the number of unsaturated chain ends is not equal to the number of aliphatic chain ends. It will be seen farther in this paper that initiation by coinitiation often is the most probable reaction scheme. Whatsoever, it must be concluded that a strong Lewis acid such as BF_3 does not allow a good control of the chain end functionalization, since we have to compromise between yield and functionalization. A comparison with the next system is illustrating.

The polymerization of 2-methylpropene was initiated by BAMEB in CH_2Cl_2 at -50°C. The Lewis acid was titanium tetrachloride. Some typical results are shown on Table 5. Despite some scatter in the results, it is clear that the yield was never complete. In the case of run 2 the lower yield is due to the fact that the azide concentration was higher than that of the Lewis acid. Runs 2 and 3 gave polydispersity indeces around 2. The result of run 1 must be discussed. It is worth noticing that the initiator (bis-1,4-(1-azido-1-methylethyl)benzene, BAMEB) is bifunctional. Consequently, in the case of a predominant step of interruption of chain growth, a polydispersity index of 1.5 is expected. This is exactly what it is observed. Run 4 was carried out in the presence of a small quantity of ditertiobutylpyridine (DtBP), but with the same conditions as run 3. It can be seen that in term of yield, the results are the same as without proton trap (run 3). However, the functionalization is much lower. This is to be assigned to the fact that DtBP interacts with the active species and modifies their reactivity. This effect was noticed several times in our laboratory. It was also found that all polymers contained chloride. It is worth mentioning that in methylene chloride the solubility of the poly(2-methyl propene) is limited. If the molecular weight obtained in methylene chloride would only result from solubility characteristics, the comparison between the results quoted on Table 5 and Table 1 shows that this is not the case, since at the same temperature (-50°C) the molecular weight is different.

Table 5
Polymerization of the system $IB/BAMEB/TiCl_4/CH_2Cl_2$, at -50°C, t = 50 min.

N°	IB M	BAMEB M ***	$[TiCl_4]$ M	Yield %	Mn D	f_{N3}	I*
1	1.1	1.10^{-2}	2.10^{-2}	92	6200	1.1	1.5
2	1.0	1.10^{-2}	1.10^{-2}	56	5500	0.5	1.8
3	1.0	1.10^{-2}	6.10^{-2}	80	5000	1.6	2
4**	1.2	1.10^{-2}	7.10^{-2}	74	6900	0.8	-

*Polydispersity index.
**In the presence of 6.10^{-3}M of DtBP.
***BAMEB = N_3-$C(CH_3)_2$-φ-$C(CH_3)_2$-N_3

A brief study was devoted to the study of small variations of the reaction conditions to see whether some improvement could be found. Various initiators were used, i.e. cumyl azide or bis-1,4-(1-azido-1methylethyl)benzene (BAMEB). The results are shown in the next table

6 (runs 1-4 with cumylazide and run 5 with BAMEB). At -60°C, the yield using $TiCl_4$ is not better than with BF_3 at -70°C.

Run 4 demonstrates once more the detrimental effect of DtBP on the functionalization. On the other hand it is interesting to note that the best functionalization was obtained for a one-to-one ratio of the initiator concentration to that of the Lewis acid (run 2). This result allows to choose among the two possible mechanisms of functionalization, predominant transfer on the azide molecule or coinitiation with the organic azide. Since the theoretical molecular weight assuming one aromatic nucleus per chain is always lower than the experimental one and since the used organic azide (based on the azide functionalization) goes through a maximum for the one-to-one ratio, these observations strongly suggest that the main role of cumyl azide is to be ionized by reaction with the Lewis acid, i.e. to behave as an initiator. Functionalization efficiency is slightly better with BAMEB than with Cum-N_3.

Table 6
Polymerization in the system 2-methylpropene (1.1 M)/
Cum-N_3(runs 1-4) or BAMEB(run5) /$TiCl_4$ (0.05 M)/CH_2Cl_2, at -60°C, t = 30 min.

N°	[-N_3]/[$TiCl_4$]	Yield %	Mn_{th}* D	Mn_{SEC}** D	f_{N3}***	Used N_3 %
1	1.7	90	725	3000	0.5	12
2	1	80	1400	2200	0.6	26
3	0.5	100	2500	3500	0.1	7
4****	1	100	1400	2500	0.2	10
5	1	80	1400	3000	1.1	36

*Assuming one cumyl-N_3 molecule per chain (no transfer).
**In eq. p.St.
***determined by IR spectroscopy.
****Experiment carried out in the presence of DtBP (10^{-3} M).

Experiment N°5, Table 6, gave a polymer having a polydispersity index of 1.5. Part of the chain ends contained chloride, since a -Cl functionality of 0.13 was measured by NMR spectroscopy. It also contained terminal double bonds, their functionality being 0.6 also measured by ^1H NMR spectroscopy.

It is interesting to notice that the results of the experiment 5 in term of yield and functionalization quoted on table 6 is practically the same as that of run 2 carried out in the same conditions of azide group concentration but with a monofunctional initiator. It also shows that the interruption of chain growth occurs at random, the polydispersity index of the polymer 5 being equal to 1.5. The comparison of the same experiment with the run 3 of table 5 carried out in similar conditions does not give hopes to get a definite improvement since a slightly lower polydispersity index is observed but with a slightly lower functionalization. Compared to the results of Table 4, the use of a this new set of conditions (Lewis acid and temperature) does not allow a better functionalization, and, besides tranfer, this can be assigned at least partly to the termination by chloride, which cannot happens with BF_3.

In order to expand the scope of this chemistry, some experiments were carried out with another pseudohalide, the isothiocanate group -NCS. It was first determined whether an alkyl isothiocyanate could initiate the polymerization of 2-methylpropene. The next table 7 describes one experiment with again 2-methylpropene and $AlEt_2Cl$ which is a rather weak Lewis acid. It was verified that in CH_2Cl_2 at -50°C it cannot initiate the polymerization of 2-methylpropene while it does when 2,4,4-trimethyl-2-isothiocyanatopentane (H-TMP-NCS) is present. The polymer was analysed by ^1H NMR and infrared spectroscopies, and the surprise came from the much higher content of thiocyanate function than that of isothiocyanate. It has been shown that isomerization of alkyl thiocyanates to isothiocyanates could be obtained, while not quantitatively, and that the rates of isomerization increased in the order of increasing stability of the carbocation derived from the alkyl group atached to the sulfur atom (11). Consequently, at equilibrium for the interchange between the two functions, the isothiocyanate must be the major function, while its relative concentration may depend to some extent upon the reaction conditions. The above observation of the polymer functionalization is in tune with the higher nucleophilicity of the sulfur atom and the higher basicity of the nitrogen atom of the thiocyanate ion. The thermodynamic equilibrium slowly establishes while polymerization proceeds.

For this polymer, the polydispersity index was low, but it was due to the low polymerization degree. The high unsaturation content shows that transfer was extensively occuring and is in tune with the preceding conclusion that the system was neither living nor controlled. It is worth recalling here that the same kind of functionalization was observed when the same type of 2-methylpropene polymerization (2-methylpropene/H-TMP-NCS/CH_2Cl_2) was tried at -50°C in the presence of ditertiobutylmethylpyridine (12). Another surprise was found in the fact that the system 2-methylpropene/H-TMP-NCS/$TiCl_4$/CH_2Cl_2 at -50°C, where the Lewis acid concentration was twice the concentration of the organic isothiocyanate, did not give functionalization, H-TMP-NCS being recovered untouched (13). It can be surprising at first sight that a strong Lewis acid ($TiCl_4$) apparently does not interact with an alkyisothiocyanate, while a weaker one such as $AlEt_2Cl$ does. It can be suggested that the sulfur atom of the H-TMP-NCS is more accessible to the aluminum atom of $AlEt_2Cl$ than to the titanium atom of $TiCl_4$. However, a comparison with another run where the concentration of $TiCl_4$ was equal to that of the same isothiocyanate gave a partly functionalized product. It shows that an excess of $TiCl_4$ allows a polymerization which can polymerize without interaction with the isothiocyanate groups, this polymerization being initiated by direct initiation (13). To this respect, the situation seems to be less interesting that the situation which prevails in the case of azide group. On the other hand, the study of the

Table 7
Polymerization of the system 2-methylpropene (IB = 0.91M)/
H-TMP-NCS/$AlEt_2Cl$/CH_2Cl_2, at -50°C, t = 50 min.*

N°	[H-TMP-NCS] M	[$AlEt_2Cl$] M	Yield %	Mn**	f_{SCN}	f_{NCS}	$f_=$***
1	0.04	0.08	54	500	0.22	0.04	0.7

*H-TMP-NCS = tBu-CH_2-$C(CH_3)_2$-NCS
**By NMR spectroscopy, based on the t-Bu chain-ends content.
***Unsaturation content, number of double bonds per chain.

model system Cumyl-NCS/TMP1/$TiCl_4$/CH_2Cl_2 at -50°C with a Lewis acid concentration twice that of the cumyl-NCS showed the formation of H-TMP-Cl and H-TMP-NCS. This shows that this isothiocyanate of the benzylic type interacts more readily with $TiCl_4$ than the alkylisothiocyanate.

II-2- Functionalizing cationic polymerization with a polydispersity index lower than two.

If a polydispersity index lower than 2, and of course as low as possible, is to be preferred, transfer and termination must be eliminated, which means that living system is required, or at least a system of « controlled polymerization ». However, if the termination by azide ion is a true termination low polydispersity indeces should not be possible. An investigation of this point was effected with two different monomers and two pseudohalides, the azide and the isothiocyanate groups. A review of some systems investigated in our laboratory provides the answer to this question.

The first one is a system in which the functionalization of poly(2-methylpropene) is carried out by exchange. Table 8 gives some informations.

Table 8
Polymerization of the system 2-methylpropene/TMSA/
$TiCl_4$/various solvents, at -70°C, t = 2 h.

N°	[IB] M	[TMSA] M	[$TiCl_4$] M	Solvent % (v/v)	Yield %	Mn_{SEC}** D	I*	f_{N3}	f_{Cl}
1	1.0	0.13	0.13	CH_2Cl_2 67 % hexane 33 %	93	7900	1.4	0.4	0.3
2	1.0	0.13	0.13	CH_2Cl_2 50 % hexane 50 %	26	8100	1.3	0.7	-

*Polydispersity index.
**In equivalent pSt.

In this system, two solvent mixtures were tried, CH_2Cl_2 with two different contents of hexane. If the first mixture gave a rather high yield, the second one gave a much lower yield of the same molecular weight but with higher azide group content. Polymers contained chloride and a small amount of terminal unsaturation. The rather low polydispersity indeces allow to raise an interesting question. If the functionalization is obtained by exchange after polymerization, and if there is some termination reaction, the polydispersity index should not be lower than 2 since the 2-methylpropene is not living in these conditions. The simplest explanation for this low polydispersity index is that functionalization is not effected after polymerization but during polymerization and that this functionalization is not a true termination. Since all polymers contain chloride function, it is proposed that terminal chlorinated chain ends are exchanging with azide groups, so that these groups are also a kind of dormant species. It will be seen below that this proposal can account for our most important observations.

Since at -70°C the system seems to give low polydispersity index, the same type of functionalization by exchange was tried in pure CH_2Cl_2 as described in Table 9. Run 1 shows that the yield was complete in these conditions. It is worth noting here that in this system initiation is due to direct initiation and probably to residual cocatalysis (14).

Table 9
Polymerization of the system 2-methylpropene (IB)/TMSA/ $TiCl_4/CH_2Cl_2$, at -70°C, t = 2 h.

N°	[IB] M	[TMSA] M	[$TiCl_4$] M	Solvent	Yield %	Mn_{SEC}** D	I*	f_{N3}	f_{Cl}
1	1.2	0.14	0.14	CH_2Cl_2	100	6300	1.3	0.6	0.3
2	0.4	0.03	0.03	CH_2Cl_2	100	3000	1.8	0.4	0.3

*Polydispersity index.
**In equivalent pSt.

As for the chain ends of the polymer corresponding to run 1, most of the macromolecules are terminated by either an azide group or a chloride group. The low polydispersity index indicates that all macromolecules could grow and that the terminal functionalization was not a termination reaction occuring at random. Run 2 deserves some comments. This experiment was approximately the same as run 1 but using a dilution factor of around 4. ^1H NMR analysis showed that the polymer contained a noticeable amount of terminal unsaturation, which showed the existence of transfer. This conclusion is in tune with the higher value of the polydispersity index. The mechanistic reason of this dilution effect is not known and is under investigation in our laboratory.

Table 10
Polymerization of the system 2-Methylpropene (1.2 M) /$HN_3/TiCl_4$ ($5.6.10^{-2}$M)/CH_2Cl_2, at -70°C, t = 30 min.

N°	[HN_3]/[$TiCl_4$]	Yield %	Mn_{th}** D	Mn_{SEC}* D	f_{N3}***	Used N_3 %
1	1.5	80	800	2500	0.4	10
2****	1.1	80	1100	2300	0.7	26
3	0.75	90	1600	2500	0.6	34
4	0.50	100	2400	3000	0.4	32

*In eq. p.St.
**Assuming one HN_3 per macromolecule (no transfer).
***determined by IR spectroscopy.
****This experiment when carried out in the temperature range -70°C -50°C give a polydispersity index of I = 1.35.

In order to show the field of application of the above conclusions, some informations must be given on a system in which initiation results from cocatalysis by HN_3.

Table 10 reports some experiments, and when the ratio $[HN_3]/[TiCl_4]$ is around 1, the polydispersity index is 1.35. Besides the azide content which is mentionned in Tables 9 and 10, all polymers contain tertiary chloride (as shown by ^{1}HNMR spectroscopy). It is clear that the same considerations as above can apply, i.e. that all macromolecules can grow up, except those which are terminated by an unsaturation. This means that terminal azide and terminal chloride are exchanging at equilibrium, and exchanging with the active species.

The conclusion drawn from these experiments is not to be considered as valid only in the case of 2-methylpropene. It was felt that this mechanism could be more general. For that reason it was decided to investigate a totally different polymerizing system, the 2-methyl-2-oxazoline in the presence of benzyl bromide in acetonitrile. It is well known that this is a living polymerization. The effect of the presence of TMSA was investigated at 80°C (15). Table 11 reports some experiments which allow to draw the main informations.

Table 11

Polymerization of the system 2-methyloxazoline/Benzyl bromide (BzBr = 0.044 M)/TMSA/ acetonitrile, at 80°C ([2-methyl-2-oxazoline] = 1.77 M).

N°	[TMSA]	t	Yield	Mn_{the}	Mn_{NMR}	Mn_{SEC}	I_p	f_{N3}
	M	h	%	*	**	***	****	%
1	0.088	24	100	3575	3700	4100	1.3	89±5
2	0.132	24	100	3575	3000	4000	1.2	100±5
3*****	0.132	48	75	4710	3000	3800	1.3	100±5

*calculated from the monomer to BzBr ratio.

**Calculated from the NMR spectrum assuming one aromatic nucleus per chain.

***Determined by SEC (H_2O, light scattering)

****Polydispersity index.

***** Polymerization carried out according to the incremental monomer addition (IMA) technique, a second monomer charge (0.59 M) being introduced 24 hours after the first one (1.77 M).

Runs 1-2 clearly demonstrate that, despite the presence of TMSA and within experimental accuracy, the polymerization was living. It must be noticed that the experimental molecular weight were reasonably close to the theoretical one given by the ratio monomer to initiator concentrations. The polydispersity indeces were low, and as a whole, the behavior was the same as published some years ago by Saegusa et al. (16). The main point is that when the TMSA concentration was sufficiently high, the functionalization was apparently complete. However, run 3 indicates that when a new charge of monomer was introduced in such a system where the azide functionalization is complete, the polymerization of the second charge did not occur, while it does in the absence of TMSA. These observations are again in tune with our conclusion that terminal azide does not propagate but can exchange with the brominated chain ends. Thus, this scheme can explain the low polydispersity index. The reason why it was possible to obtain at the same a complete polymerization and a high level of functionalization is that the rate of polymerization is higher than that of functionalization. A complete analysis of this system is going to be published (15).

Similarly to the context of the organic azide, the polymerization of 2-methylpropene initiated by bis-1,4-(1-isothiocyano-1-methylethyl)benzene, called hereafter dicum-NCS, in the presence of $TiCl_4$ was tried at -70°C. One typical result is quoted on the next table 12.

Table 12

Polymerization of the system 2-methylpropene (IB)/dicumyl-NCS/$TiCl_4$/CH_2Cl_2, at -70°C.

N°	[IB] M	[dicum-NCS] M	[$TiCl_4$] M	Yield %	I***	f_{NCS}*	Mn_{SEC}** D
1	1.34	$1.5.10^{-2}$	$7.9.10^{-2}$	100	1.3	0.1	4900

*Determined by NMR spectroscopy (peak at 1.59 ppm= $-CH_2-C-NCS$).

**In eq. p.St.

***Polydispersity index.

It can be seen that in the conditions selected for this experiment, the polymerization yield is complete, but the functionalization by the isothiocyanate group was poor (10%) besides a very small amount of thiocyanate group. This last point shows that this experiment was carried out in such conditions that the thermodynamic equilibrium of exchange on chain ends was reached. NMR analysis revealed that the polymer contained an important fraction of tertiary chloride and no terminal unsaturation. This last observation is consistent with the low polydispersity index, since there was no transfer. Once again the equilibrium between chlorinated chain ends and their functionalized counterparts explains the low polydispersity index with a complete yield.

What can be learnt from this general survey ? It was first shown that functionalization can be observed with at least two pseudohalides, besides one experiment using CN published long time ago (17). Not only the synthesis of functionalized oligomers can be carried out in a one batch process, but also a control of the reaction can be obtained from adjustment of the conditions. This is particularly clear if the polymerization of 2-methylpropene is examined in the presence of an initiator or a pseudohalide donor such as TMSA.

An important observation was that a control of the molecular weight of PIB oligomers was obtained at sufficiently low temperature, i.e. at -70°C (using $TiCl_4$), and at 80°C for 2-methyl-2-oxazoline. These conditions are generally the ones which prevail obtaining controlled polymerization. Since in the case of $TiCl_4$ the chain ends were always containing at the same time tertiary chloride and a pseudohalide group, the low polydispersity index at complete yield can only be explained by an equilibrium involving both chain ends, according to the following scheme (mixed initiation or not):

Cocatalysis Coinitiation Direct Initiation

$$\Downarrow$$

$$R\text{-}(\text{-}M\text{-})_n\text{-}X + MtX'_n \Leftrightarrow R\text{-}(\text{-}M\text{-})_{n-1}\text{-}M^+,C^- \Leftrightarrow R\text{-}(\text{-}M\text{-})_nX' + MtXX'_{n-1} \quad (A)$$

$$\Downarrow$$

polymer

where X is a pseudohalide, X' is a halide coming from the Lewis acid MtX'_n, C^- is a counteranion which contains a pseudohalide anion X^-, and $MtXX'_{n-1}$ is a Lewis acid in which a halide anion has been replaced by a pseudohalide anion. The interest of the equilibria (A) is that the polymer product is made uniform due to these exchange reactions which cannot be established with azided chain ends when the coinitiator is a too strong Lewis acid (BCl$_3$,) or when multiple initiation can overcome this effect (BF$_3$).

It is important to note that a simple exchange of counteranion between different active species cannot account for I<2 for monofunctional growth, even if it is likely that the exchange is operating through the active species, as shown by equation (A) above, and not directly with the covalently bound pseudohalide X.

Now, the question is to know whether the chain end functionalized by the pseudohalide is able in itself to give access to a controlled polymerization without the presence of a chloride chain end. One system seems to indicate that it is possible to find conditions leading to controlled polymerization without any measurable amount of chlorinated chain ends. The main characteristics of this system were described somewhere else (18). In this paper, the polymerization of 2-methylpropene was studied initiated by BAMEB in the presence of AlEt$_2$Cl in polar medium. It was shown that this system was reasonably living at -50°C or below, the number of macromolecules being equal to the number of initiator molecules (18). The next table 13 shows some experiments.

Table 13

Polymerization of 2-methylpropene in CH$_2$Cl$_2$ at -50°C initiated by the system BAMEB/AlEtCl$_2$

N°	[IB] M	[BAMEB] M	[AlEt$_2$Cl] M	Yield %	I**	f$_{N3}$***	Mn$_{SEC}$* D
1	0.053	$2.2.10^{-3}$	$1.7.10^{-2}$	98	1.3	2.0	1650
2	0.22	$2.2.10^{-3}$	$1.7.10^{-2}$	100	1.3	2.1	5800
3	0.84	$1.9.10^{-3}$	$1.5.10^{-2}$	98	1.3	2.1	24300

*In eq. p.St.

**Polydispersity index.

***determined by IR spectroscopy.

The functionalization of the macromolecules was perfect within experimental accuracy, and more particularly no chlorine atom was detected in conditions where the polymerization was controlled. It is then clear that in some conditions the presence of chlorinated termini is not a stringent requirement for obtaining a good molecular weight control. It was shown above that their presence participates to this control, while it is of course detrimental to the functionalization. However, it is then clear that the azide group can provide at the same time the dormant and the active species, providing specificity and selectivity. Most probably, the same situation could be met using the other pseudohalides, in some specific conditions which remain to be determined.

III- Conclusion

The use of additives containing a mobile pseudohalide function opens the way to functionalized oligomers in a one step synthesis from the monomer either through coinitiation or by exchange reaction. When the systems of 2-methylpropene polymerization described above were examined, it has been shown that the results varied progressively from systems where the functionalization was negligible or present in minor proportion (BCl$_3$, BF$_3$), to systems giving access at the same time to a fairly good functionalization in a one-batch process and to good molecular weight control ($AlEt_2Cl$). It is interesting to note that 2-methylpropene is not the only monomer susceptible to give functionalized oligomers by this technique.

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