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Synthesis of Polymers Containing Pseudohalide Groups by Cationic Polymerization. 8.[†] Thiocyano- and Isothiocyano-Functionalized Poly(2-methylpropene) Using 2-Isothiocyano-2-phenylpropane as Initiator

C. Descours-Michallet,[‡] H. Cheradame,* and F. J. Chen[§]

Université d'Evry Val d'Essonne, LPCB-CNRS, U.M.R. 27, 94320 Thiais, France

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Our previous work described the introduction of pseudohalide functions onto a polymer backbone by cationic polymerization.[1-3] Recently, using the same type of chemistry, we found a way leading to poly(2-methylpropene) (PMP) functionalized at the chain ends by isothiocyanate and, more surprisingly, thiocyanate groups.[4] Coinitiation chemistry using 2-isothiocyano-2,4,4-trimethylpentane (ITP) gave a mixture of various chain ends, but in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (DBMP), the specificity of the functionalization was improved, the thiocyanate chain end becoming the major product. According to published work,[5] it could be possible to enhance the functionalization specificity and the polymerization yield using a more easily ionizable initiator, 2-isothiocyano-2-phenylpropane (IPP), similarly to the recently published work with the azide function.[6]

Thus, initiator, 2-isothiocyano-2-phenylpropane, was synthesized according to the following reaction scheme:[7]

$$\mathrm{PhC(CH_3){=}CH_2 + HSCN \xrightarrow{TiCl_4} PhC(CH_3)_2NCS}$$

Thiocyanic acid was prepared according to the following reaction:

$$\mathrm{2NaHSO_4 + NH_4SCN \rightarrow HSCN + Na_2SO_4 + NH_4HSO_4}$$

We used the previously described technique[3,4] for the purification of the various reactants, monomer, solvent, and additive, such as 2,6-di-*tert*-butyl-4-methylpyridine. The reaction product, 2-isothiocyano-2-phenylpropane, was obtained by the fractionation of the system on a silica column, controlled by gas chromatography on an SE30 column. Polymerization catalyst ($TiCl_4$) was used as a molar solution in CH_2Cl_2.

We describe here the initiation of 2-methylpropene polymerization by the IPP–$TiCl_4$ system. The results of a characteristic experiment are described in the first line of Table I. The polymerization yield is not better here (49%) than with ITP (60%).[4] This incomplete yield indicates that these two systems are similar. Since 80% of the macromolecules contain one phenyl ring, it is clear that the initiation efficiency of IPP is high, while that of ITP was low.[4] The fact that the initiation efficiency of IPP is higher supports our view on the higher ionization degree of the IPP–$TiCl_4$ complex. The high initiation efficiency of IPP is also confirmed by the fact that only a small quantity of IPP was found in the solvent after polymerization quenching.

The clear increase in nitrogen-containing function is also in tune with our previous expectation that a more dissociated active species would favor this type of terminal chain end. ^{1}H NMR spectroscopy allows us to determine the presence of *tert*-butyl groups for a content of 9400 g/mol of *tert*-butyl group and tertiary chloride groups corresponding to a content of 2500 g/mol (Figure 1). The tertiary isothiocyanate functions are identified by their two methyl groups giving a peak at 1.49 ppm, similar to the chemical shifts of ITP.[4] Since the polymer does not contain any terminal unsaturation, its *tert*-butyl groups are not produced by transfer but rather by cocatalysis by water. The absence of terminal unsaturation here shows that the more dissociated ion pairs generated by the initiating system with IPP do not give proton transfer, as in the presence of hindered pyridine with the ITP initiator,[4] and can be explained by the assumption that the more dissociated, the lower the extent of proton extraction from the positive moiety by the counteranion. The high amount of tertiary chloride terminal function is similar to the case of initiation by ITP in the presence of DBMP.

Some polymerizations initiated by IPP were carried out in the presence of DBMP. The results of a characteristic experiment are shown Table I. For this experiment, the mixing sequence was DBMP, CH_2Cl_2, MP, IPP, and $TiCl_4$. The polymerization yield is higher in the presence of DBMP than without (Table I). The polymerization yield of this second experiment (66%) includes not only the polymer cleaned for further analysis (16%) but also the small molecular weights soluble in the solvents used for this cleaning operation (50%). Cocatalysis, which leads to higher molecular weight, is probably totally absent with this type of initiation. Not only the nitrogen-containing functionality is high but the specificity is quasi-total, since the isothiocyanate function represents not more than 3% of the nitrogen-containing functions. Figure 2 shows the infrared spectrum of the polymer after cleaning by dissolution and precipitation. Figure 3 shows the SEC chromatogram of the same polymer. The polydispersity index is low. Actually, this index is equal to 1.2, which is of the same order of magnitude as that of the polymer obtained without DBMP. It is worth noting that the low polydispersity index could not be only ascribed to a fractionation effect of the cleaning operation, since the same technique was applied to the polymer initiated by the ITP–$TiCl_4$ system and a high polydispersity index was measured.[4]

^{1}H NMR analysis of the polymer after cleaning allows us to determine an aromatic nuclei content of 1500 g/mol and a very low *tert*-butyl group content of the order of 34 000 g/mol. The two contents using the functions which are "beginning" a macromolecule (*tert*-butyl and phenyl ring) allow us to calculate an average number molecular weight by NMR spectroscopy of 1400. The very high aromatic nuclei content confirms the high initiating efficiency of IPP in the presence of DBMP and the quasi-absence of cocatalysis. Surprisingly, this last analysis shows a small content of terminal disubstituted double bonds corresponding approximately to 34 000 g/mol. It is tempting to assign this terminal unsaturation to the polymer having a *tert*-butyl group at the other end. This fraction of low amount could be due to proton transfer. However, this type of polymer was not found in the absence of DBMP. The reason for such a structure can simply be assigned to residual proton transfer occurring on solvated ion pairs present in larger amount when polymerization is carried out in the presence of DBMP.

The proton NMR spectrum of the cleaned polymer also shows the presence of tertiary chloride chain ends, similarly to the structure of the polymer synthesized by initiation with the ITP–$TiCl_4$ system in the presence of DBMP.[4]

[†] Part 7: cf. ref 4.

[‡] EFPG, B.P. 65, 38402 Saint Martin d'Hères, France.

[§] Paramins, Exxon Chemical, P.O. Box 536, Linden, NJ 07036.

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Table I
Polymerization of 2-Methylpropene (MP) Initiated by the IPP–$TiCl_4$ System in CH_2Cl_2 at −50 °C in the Presence of 2,6-Di-*tert*-butyl-4-methylpyridine (DBMP)[a]

DBMP, mol/L	MP, mol/L	IPP, mol/L	$TiCl_4$, mol/L	Y, %	M_n[b] NMR	f_{NCS},[b] % IR	f_{SCN},[b] % IR	f_{Ph},[b] %
0	1.0	0.045	0.045	49	1700	11	20	80
0.035	0.90	0.04	0.04	66	1300	2	60	96

[a] Reaction time = ca. 15 min. [b] Polymer precipitated twice in acetone. The three functionalities are calculated using the M_n determined by functional analysis from the NMR spectrum.

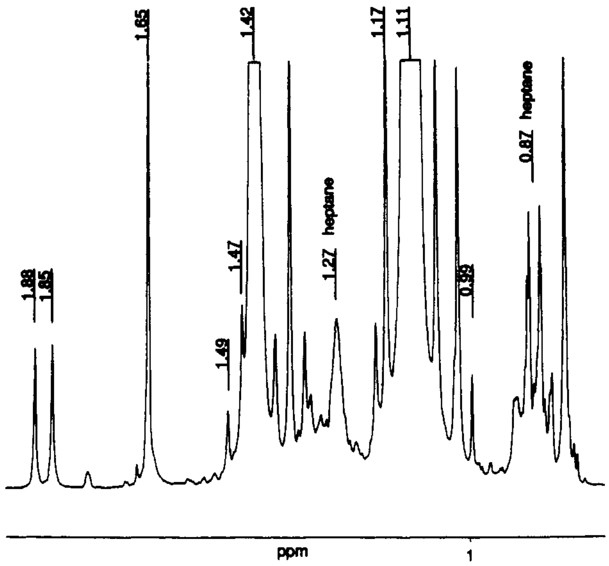

Figure 1. ^1H NMR spectrum of the poly(2-methylpropene) initiated by the IPP–$TiCl_4$ system in CH_2Cl_2 at −50 °C.

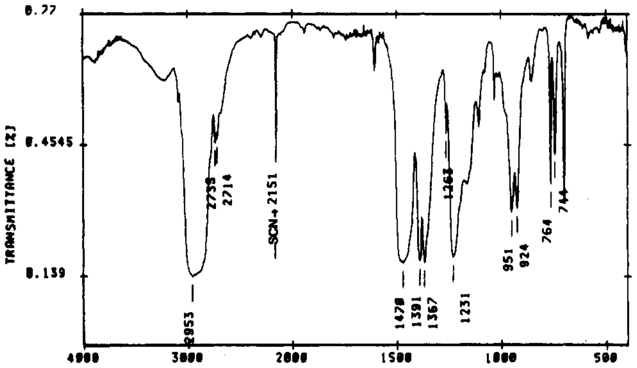

Figure 2. Infrared spectrum of the poly(2-methylpropene) initiated by the IPP–$TiCl_4$ system in CH_2Cl_2 at −50 °C in the presence of 2,6-di-*tert*-butyl-4-methylpyridine.

However, the amount of tertiary chloride is still high, since from the spectrum a content of 2500 g/mol is measured. The amount of thiocyanate functions corresponds to 2200 g/mol. Combined with the above figures of terminal chloride and terminal disubstituted unsaturation, we find an average number molecular weight of 1100. Thus, the average number molecular weight of the cleaned polymer was taken as the average of the two figures given by the "initial" and "terminal" functions (i.e., M_n = 1300).

Conclusion. This work establishes that, according to previous indications,[4] DBMP interacts with the active species and modifies the nature of the termination reactions.[4] It seems that the solvation of the active species and their dissociation increase the extent of the reaction leading to the formation of the carbon-to-sulfur bond. More importantly, this work confirms that in the presence of isothiocyanate groups the cocatalytic initiation due to residual water is at least minimized or eliminated. This selectivity of initiation could be a precious tool for further study aiming at the synthesis of well-defined oligomers and demonstrates the potential of "initer" systems. We were hereby able to obtain PMP at least partly under the form of an asymmetric ditelechelic polymer, having around 96% of macromolecules beginning at one end by a phenyl ring, and around 60% terminated by a thiocyanate group. This is the first report of a PMP functionalized by a carbon-to-sulfur bond by direct synthesis from the monomer at such an efficiency.

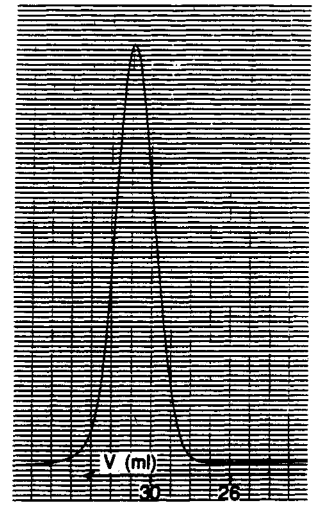

Figure 3. SEC chromatogram of the poly(2-methylpropene) initiated by the IPP–$TiCl_4$ system in CH_2Cl_2 at −50 °C in the presence of 2,6-di-*tert*-butyl-4-methylpyridine. This polymer was precipitated twice in acetone.

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References and Notes

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