Macromolecules 1993, *26*, 2297–2302

Synthesis of Polymers Containing Pseudohalide Groups by Cationic Polymerization. 5. Study of Various Aspects of the 2-Methylpropene Polymerization Coinitiated by Hydrazoic Acid[1]

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Received August 3, 1992; Revised Manuscript Received December 29, 1992

ABSTRACT: It is possible to functionalize poly(2-methylpropene) with nitrogen-containing functions using a suitable coinitiator, here hydrazoic acid, in the presence of boron trifluoride or diethylaluminum chloride in methylene dichloride. Polymerization at −50 °C initiated by boron trifluoride showed the same general phenomenology as in the case of titanium tetrachloride initiation: the best functionalization efficiency for a one to one molar ratio of coinitiator/Lewis acid. Poly(2-methylpropene) with an azide group functionality of 0.9 was obtained by initiation with diethylaluminum chloride. In the case of this Lewis acid the initiating efficiency of hydrazoic acid was low. Polymerizations performed at room temperature, initiated by the system hydrazoic acid–titanium tetrachloride, supported previous mechanistic interpretation, such as unsaturated macromer dimerization.

Introduction

This paper is the fifth of a series aiming at opening a field of new monomers, polymers, and copolymers containing functions of the pseudohalide type and dealing with cationic polymerization. We studied first the conditions to be used for nucleophilic monomers, such as cyclic ethers containing azide groups, to allow cationic polymerization and copolymerization.[4,5] Later we demonstrated that alkenyl monomers, such as vinyl ethers, styrene, and 2-methylpropene,[6–8] can be polymerized in the presence of molecules containing pseudohalide groups, such as isothiocyanate,[9] nitrile, and azide functions, despite the fact that these functions contain nucleophilic sites which could compete with the monomer to react with the electrophilic initiating species. In the case of the less nucleophilic monomers (styrene and 2-methylpropene), it was shown that cationic polymerization could take place provided that the Lewis acid ($TiCl_4$) concentration was equal to or higher than that of the azide group. This effect was assigned to a complexation between the Lewis acid and the azide group. Direct functionalization of poly(2-methylpropene) (PMP) was obtained by polymerizing the monomer in the presence of a suitable initiator such as hydrazoic acid or cyanhydric acid.[10] It was shown that 2-methylpropene polymerization carried out in the presence of hydrazoic acid could produce monoazido-terminated oligomers with a functionality around 0.7. This result was encouraging and prompted us to investigate the scope of this chemistry which allowed, for the first time, the production by direct functionalization of PMP end-capped by a carbon-to-nitrogen bond, without the need of either further functionalization or even added end-capping chemistry. This paper presents some results aiming at the appraisal of the potential of this new chemistry.

Results and Discussion

Table I
2-Methylpropene Polymerization Coinitiated by Hydrazoic Acid in the Presence of Boron Trifluoride[a]

no.	$10^2[BF_3]$, M	[IB], M	Y, %	10^4A, mol·g^{-1} [b]	M_n	f[c]
1	4	0.95	<100	1.5	1300	0.6
2	1.6	1.12	100	0.9	1600	0.2

[a] The polymerization temperature was −50 °C, the solvent was CH_2Cl_2, and the hydrazoic acid concentration was 4×10^{-2} M. [b] Azide content expressed in moles of N_3 per gram of PMP. [c] Functionality expressed as the number of azide functions per PMP macromolecule.

1. Coinitiation of the 2-Methylpropene Polymerization by Hydrazoic Acid in the Presence of Boron Trifluoride. In the preceding paper, initiation was performed with titanium tetrachloride in the presence of hydrazoic acid. In order to expand the scope of this functionalization process with different Lewis acids, boron trifluoride was used, and some results are shown in Table I. The two experiments described in Table I clearly show characteristics the same as those of $TiCl_4$ initiation.[10] The higher azide functionalization was obtained in the case of a one-to-one initiator-to-Lewis acid molar ratio (experiment no. 1), and an excess of hydrazoic acid is detrimental to the functionality. Polymer no. 1, Table I, obtained with a yield slightly lower than 100%, was examined according to the methods described in ref 10. Its infrared spectrum is shown in Figure 1. From this figure the azide content of this polymer was calculated to be equal to 3.5×10^{-4} mol of azide group/g of polymer. Polymer no. 1 was also carefully checked by NMR spectroscopy according to the data already published[10] and the best results found in the literature.[11,12] Its protonic spectrum (Figure 2) shows many features which are not totally understood. However, the peak at 1.33 ppm, which was at least partly assigned to the *gem*-dimethyl group close to the terminal azide group,[10] allowed the determination of the azide content by NMR spectroscopy. This content was found to be equal to 3.6×10^{-4} mol of azide group/g of polymer. Whilst the accuracy of such a determination is probably worse than that of infrared spectroscopy, the agreement is good. This spectrum (Figure 2) also shows the characteristic resonance of the unsaturated protons of terminal disubstituted double bonds at 4.64 and 4.84 ppm. No other resonances characteristic of the various possible unsaturations were found. Consequently, it was considered that this terminal disubstituted double bond and the azide group were the only functions which were produced by the macromolecular chain breaking process. According to this conclusion, an average number of molecular weight of 1300 was calculated. At the other end of the macromolecule a *tert*-butyl group is expected, according to this chemistry. The spectrum, Figure 2, shows its resonance at 0.99 ppm. Its intensity

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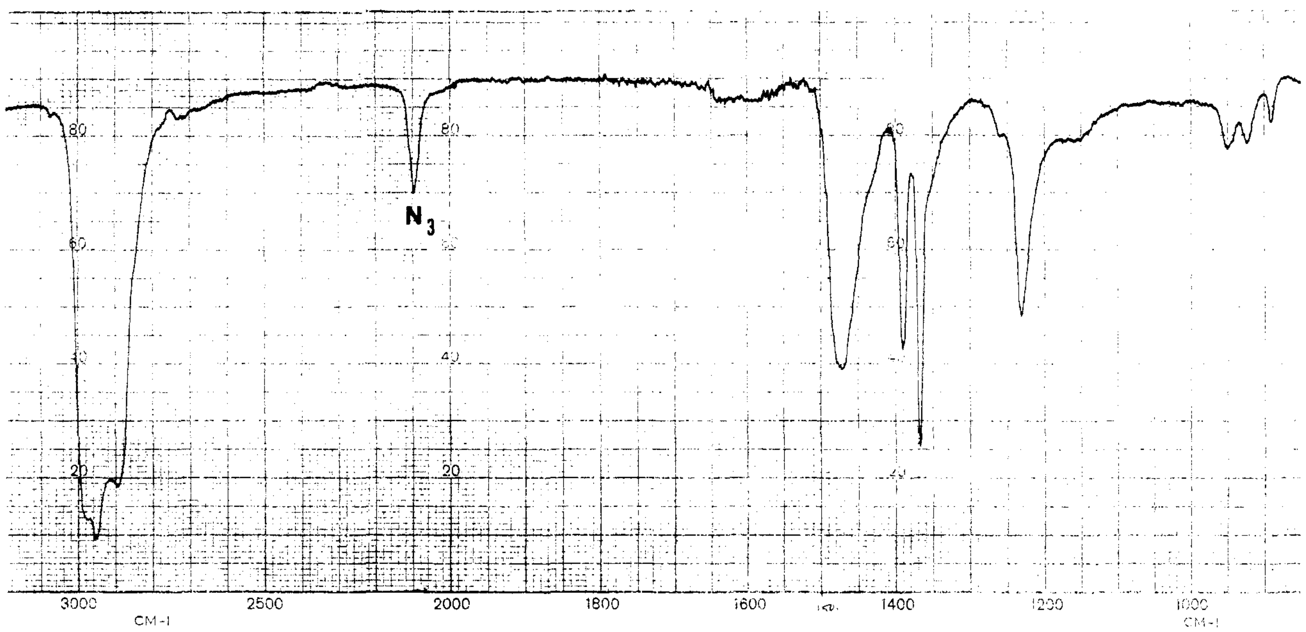

Figure 1. Infrared spectrum of polymer no. 1, Table I, showing the presence of the azide band at 2100 cm^{-1}.

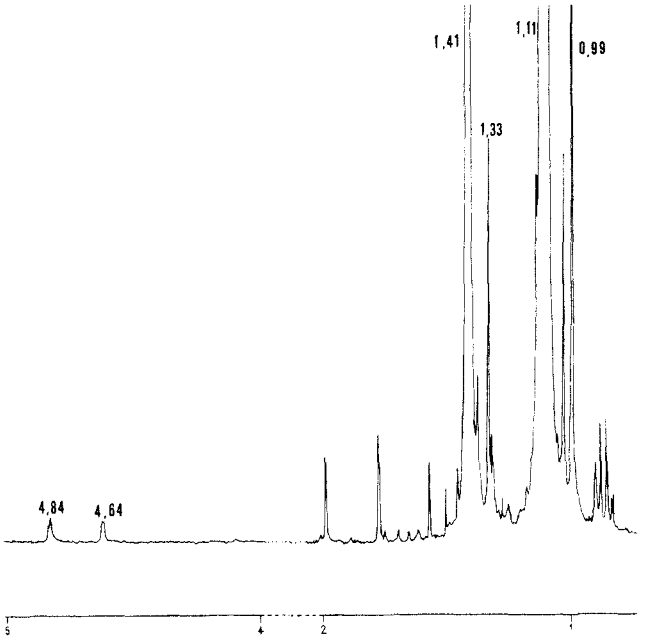

Figure 2. ^{1}H NMR spectrum of polymer no. 1, Table I, showing at 4.64 and 4.84 ppm the characteristic resonances of the terminal disubstituted double bonds and at 1.33 ppm the resonance of the methyl groups of the tertiary azide chain end.

also allows the calculation of an average number molecular weight of 1300. Of course, the agreement with the above calculation supports our interpretation.

Experiment no. 2, Table I, gives a result which also shows the detrimental effect of an excess of hydrazoic acid on the functionality. The azide functionality was only 0.2, before and after cleaning the oligomers. This experiment can be compared to experiment no. 3 of Table I in ref 10, initiated by $TiCl_4$, while conditions are slightly different. According to the discussion presented in ref 10, this low azide functionalization of this polymer is assigned to the excess of hydrazoic acid.

This short investigation allows one to conclude that the PMP functionalization by coinitiation discovered in the case of cationic polymerization initiated by $TiCl_4$ is a phenomenon which could be generalized to some other Lewis acids.

Table II
2-Methylpropene Polymerization Initiated by the System Hydrazoic Acid–AlET$_2$Cl in Methylene Dichloride^a

no.	$10^3[HN_3]$, M	$10^3[AlEt_2Cl]$, M	[IB], M	Y, %	$M_n{}^b$	$M_n th^d$	I^c
1	22	22	0.48	100	6 500	1200	2
2	9	9	0.22	100	37 500	1400	1.4
3	9	11	0.12	100	58 000	750	1.2
4	9	10	0.96	42	84 000	6000	1.3
5	10	10	0.9	75	37 000	5000	1.5

^{a} Temperature, −50 °C; CH_2Cl_2 solvent. ^{b} Determined by SEC. ^{c} Polydispersity index. ^{d} Calculated from the molar ratio monomer/HN_3.

2. Coinitiation of the 2-Methylpropene Polymerization by Hydrazoic Acid in the Presence of Diethylaluminum Chloride. The polymerization of 2-methylpropene initiated by coinitiation by hydrazoic acid in the presence of diethylaluminum chloride was also studied. The results are shown in Table II, which describes the initial conditions and some results such as polymerization yield and molecular weight. The reaction duration was between 5 and 10 min, according to the thermograms, but an induction period was noticed. All reaction products exhibited, as shown by infrared spectroscopy, the absorption characteristic of the azide group. In Figure 3, the infrared spectrum of sample 1, Table II, is displayed. In this case the functionalization was around 0.9. The molecular weights were in general too high for an accurate determination of the azide content. Table II shows that the system HN_3–$AlEt_2Cl$ in methylene dichloride gives a much higher molecular weight than expected from the molar ratio of monomer to initiator. This result shows that in these conditions hydrazoic acid has a low initiating efficiency. However, when the functionality is close to one, as in the case of experiment no. 1, the initiating efficiency can be considered as the fraction of the initiator which was effectively used to initiate polymerization. The high functionality obtained in the case of experiment no. 1, Table II, is probably to be assigned to the high concentration of the initiating system. At this point, the accuracy of the IR determination of the azide content is worth commenting on. This determination makes use of some characteristic absorption of the polymer backbone as internal standard.[10] The accuracy on the functionality

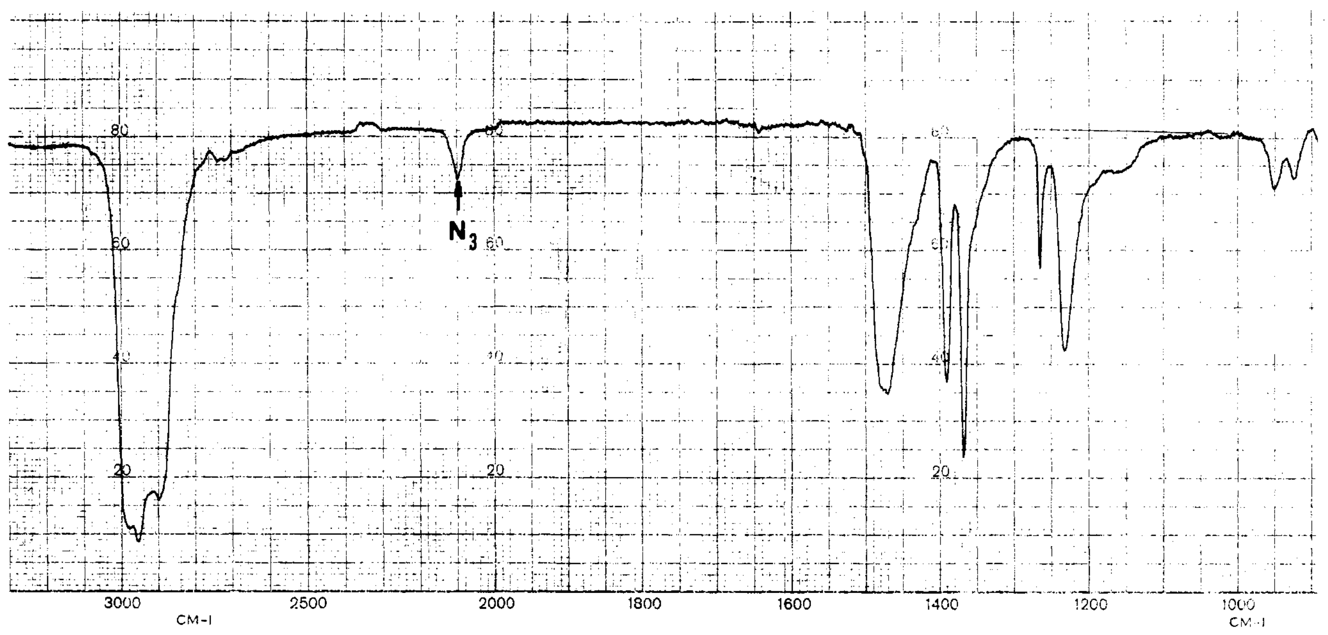

Figure 3. Infrared spectrum of polymer no. 1, Table II, showing the absorption of the azide group at 2100 cm^{-1}.

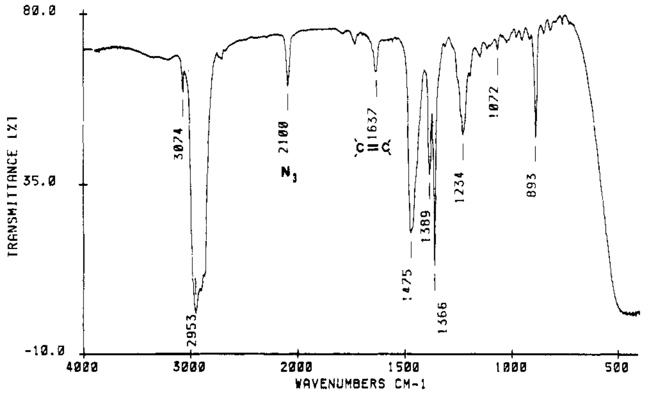

Figure 4. FTIR spectrum of polymer no. 2, Table III. A band at 1637 cm^{-1} shows the importance of the unsaturation content.

for low molecular weight samples is of the order of 10%, resulting mainly from the accuracy on the molecular weight determination.

SEC analysis allowed the determination of the molecular weight distributions of some polymers: sample 1 (polydispersity index $I = 2$), sample 2 ($I = 1.4$), and sample 4 ($I = 1.2$). The SEC chromatogram of sample 4 is shown in Figure 4. In general, the higher the molecular weight, the lower the polydispersity index. This finding is not explained at present.

From these results it is clear that hydrazoic acid can play the role of initiator for 2-methylpropene polymerization initiated by diethylaluminum chloride. It is worth noting that some experiments have incomplete yields. It could be assumed that hydrazoic acid reacts with diethylaluminum chloride according to the reaction

$$HN_3 + Et_2AlCl \rightarrow EtH + EtAlClN_3$$

then hydrazoic acid is consumed, and the extent of the polymerization depends on the relative rates of polymerization initiation and of hydrazoic acid consumption. These rates probably depend on experimental conditions such as rate of mixing, temperature, and so on. The reaction above produces azidoethylaluminum chloride in which the aluminum atom should be more acidic than that of the starting aluminum compound. It is possible that the active Lewis acid is the one produced by this reaction. Thus, the induction period could result from the lack of initial Lewis acid sufficiently strong to initiate polymerization and from the time required to produce it in situ.

Table III
2-Methylpropene Polymerization Initiated by the HN_3–$TiCl_4$ System at Room Temperature in CH_2Cl_2

no.	$[HN_3]$, M	t, min	M_n[a]	F_{az}[b]	I[c]
1	5×10^{-2}	2	400	0.08	1.84
2	5×10^{-1}	2	300	0.06	1.75
3	1	2	250	0.1	2.1
4	5×10^{-2}	60	250	0.2	1.35

[a] Measured by SEC. [b] Functionality in azide group, expressed as the number of azide groups per macromolecule. [c] Polydispersity index determined by SEC.

3. Direct Functionalization of Poly(2-methylpropene) at Room Temperature and Macromer Dimerization. It was of interest to investigate the potential of this type of functionalization at higher temperatures than that used before (−50 °C).[10] We decided to determine the main feature of this system at room temperature. Polymerization equipment and the procedure were already described for 2-methylpropene polymerization.[10] The reactor was designed to allow polymerizations under pressure. For all polymerizations discussed in this section, the 2-methylpropene initial concentration was 1.125 M and titanium tetrachloride concentration was 5×10^{-2} M. The hydrazoic acid concentration was varied as shown in Table III, which also gives some typical results. For all polymerizations described Table III, the yield was 100%. The azide content was determined by infrared spectroscopy. The infrared spectra of the polymerization products always showed a strong absorption bond at 1637 cm^{-1}, characteristic of unsaturation. The infrared spectrum (FTIR) of polymer no. 2, Table III, is shown in Figure 5. The average number molecular weights were determined by SEC. A typical chromatogram (for polymer no. 2, Table III) is shown in Figure 6. The molecular weight distribution is multimodal, and this aspect of our result could be explained by assuming that, taking into account the low molecular weight of this sample ($M_n = 300$), this chromatogram shows the different oligomers separated by the chromatographic process.

From Table III, the following information can be obtained: The comparison between experiments 1 and 4

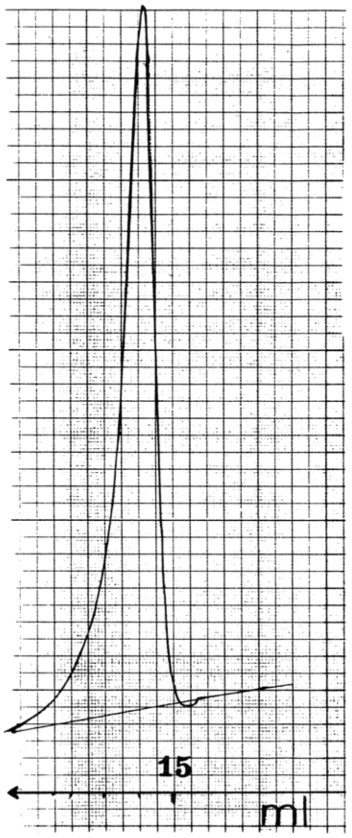

Figure 5. Size exclusion chromatogram of polymer no. 2, Table III, showing the oligomer distribution.

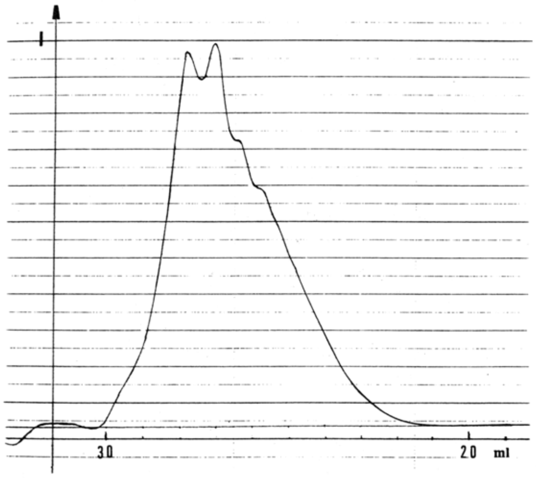

Figure 6. SEC chromatogram of sample no. 4, Table II.

shows that the hydrazoic acid concentration has no influence on the molecular weight. Experiments 1–3 show that an increase by a factor of 20 in hydrazoic acid concentration did not bring about a significant increase in the azide functionality. This functionality is rather increased by a longer reaction duration, i.e. a longer time of contact between the oligomers and the hydrazoic acid (60 min, experiment 4), since the three first experiments demonstrated that the polymerization is over within 2 min. This is in agreement with previous findings in which we demonstrated that 2-methylpropene oligomers can be totally functionalized in these conditions in 1 day, but with a higher hydrazoic acid concentration.[10] Altogether, these experiments show that the functionality is low and that this procedure cannot be used to obtain azido-terminated poly(2-methylpropene) with a good yield for functionalization.

Analysis of the above oligomers by NMR spectroscopy deserves more comment. The different structures of various unsaturations can be analyzed by proton NMR spectroscopy. It was explained in the preceding paper why some macromolecules have a *tert*-butyl group at both ends (due to macromer dimerization) and also why the hindered tertiary carbocation deprotonates giving either an internal trisubstituted double bond or a methylidene group.[10] In the present study, it is difficult to use the terminal *tert*-butyl groups on the NMR spectra since they are mixed with the protons of the methyl type of the main chain, due to the fact that molecular weight is very low. Figure 7, which displays the aliphatic portion of the spectrum of the same polymer no. 4 as in Figure 8, illustrates this problem. Figure 8 shows the unsaturated portion of the spectrum of polymer no. 4, Table III. As already explained in our preceding paper,[10] the terminal trisubstituted unsaturation gives a peak at 5.08 ppm, and the one of the disubstituted type two peaks at 4.6 and 4.8 ppm. The internal unsaturation of the disubstituted type gives peaks at around 4.72 and 4.73 ppm, while the one of the trisubstituted type is seen at ca. 5.05 ppm. The presence of these peaks confirms the simple reaction scheme previously presented.[10] This scheme implies the usual transfer reactions giving terminal unsaturations and dimerization reactions on these terminal unsaturations. Thus, it is clear that when an azide group is borne by the oligomer this latter contains no unsaturation, and this is the consequence of the fact that the active species can either deprotonate or incorporate an azide group. The composition of the different samples described in Table III is given in Table IV. Table IV shows a relatively good agreement between the average number molecular weights determined either directly from size exclusion chromatography analysis or spectroscopically from infrared and

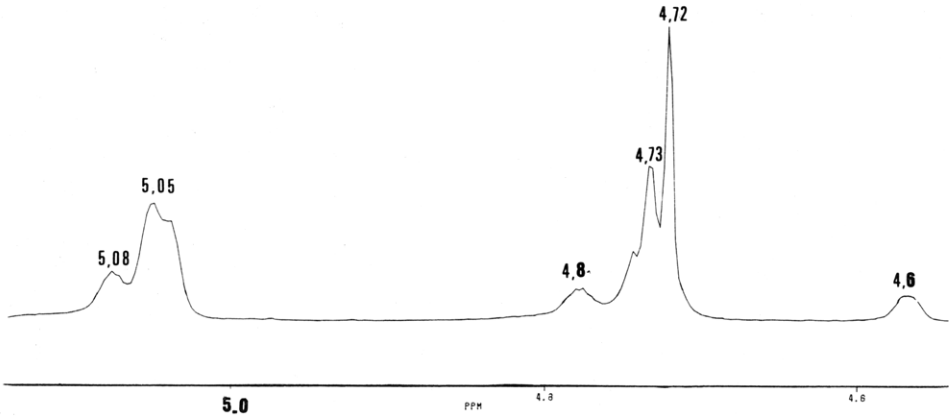

Figure 7. ^{1}H NMR of the region of the unsaturated protons of the spectrum of polymer no. 4, Table III.

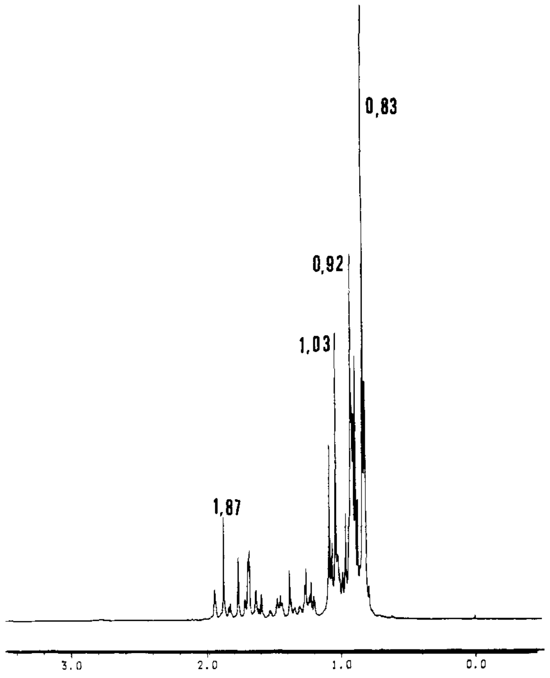

Figure 8. ^{1}H NMR of the region of the aliphatic protons of the spectrum of polymer no. 4, Table III.

Table IV
Composition of 2-Methylpropene Oligomers Obtained by Coinitiation with Hydrazoic Acid in the Presence of Titanium Tetrachloride at Room Temperature

	amt of term. unsat, mol/g × 10^4		amt of intern unsat, mol/g × 10^4		azide cont (IR), mol/g × 10^4	M_n	
no.	disub	trisub	disub	trisub		SEC	Sp[a]
1	3.88	6.66	5.95	8.47	2.08	390	370
2	8.70	7.52	13.83	8.33	2.05	280	250
3	6.07	9.71	9.62	12.64	4.61	270	240
4	3.42	5.18	12.66	18.63	8.2	250	210

[a] Average number molecular weight determined by spectroscopy and calculated from infrared (azide content) and NMR spectroscopy (unsaturation content).

NMR data. It is worth recalling here that the spectroscopic determination makes use of the assumption that there is only one double bond or azide group per macromolecule. Despite this rather good agreement, the number calculated from spectroscopic measurements is systematically lower than that given by direct SEC determination. The reason for such a behavior is that the molecular weights are at the lower limit of the validity of the SEC determination. Supporting this conclusion is the fact that the difference between the two molecular weight determinations increases when the molecular weight is decreasing.

A point of interest is the very large amount of internal unsaturation obtained for these oligomers synthesized at room temperature. This content amounts to 54% of the macromolecules synthesized within a 2-min duration. Sample no. 4 has an internal unsaturation content of 66%. Since this sample also has the lowest unsaturation content of the disubstituted terminal type and the highest azide content, it could be concluded that, after the end of the polymerization process, more hydrazoic acid addition and more dimerization occurred from these disubstituted terminal unsaturations. Sample no. 4 has the lowest polydispersity index ($I = 1.35$). Polymer recovery can also bring problems since the smallest molecules are easily lost, being a significant part of the distribution. It must be noticed that sample no. 4 has also the lowest content of trisubstituted terminal unsaturations. This probably means that this type of unsaturation undergoes an isomerization reaction into a disubstituted structure at a low rate before further addition of hydrazoic acid or dimerization.

After 2 min of polymerization the samples already contained more than 50% oligomer, resulting from oligomer dimerization, as calculated from the figures shown in Table III. This fact indicates that this side reaction proceeds at a high rate at room temperature in these conditions and confirms the observation done for polymerization carried out at −50 °C in the presence of titanium tetrachloride. This part of the work brings a clear demonstration that macromer dimerization could be a major chemical event, as already pointed out in the preceding paper.[10]

Conclusion

The present paper discloses the result that coinitiation by hydrazoic acid, discovered in the case of $TiCl_4$-initiated cationic polymerization of 2-methylpropene, is also observed in the case of boron trifluoride and diethylaluminum chloride. Apparently, transfer reactions proceed at sufficiently low rates so as to observe a non-negligible part of the poly(2-methylpropene) in the form of azido end-capped macromolecules. A functionality of 0.9 was even observed in the case of diethylaluminum chloride. It is clear that this system should be more thoroughly investigated. It was also confirmed that dimerization of macromers could be an important chemical event, as shown by the analysis of polymers obtained in the case of $TiCl_4$ initiation.

It was the first time that functionalization of poly(2-methylpropene) was achieved by coinitiation, and it is clear that we only covered a small part of this new field of functionalization. These results raise an important question which is whether this functionalization chemistry could be extended to coinitiation by a suitable organic molecule bearing a pseudohalogen group, thus leading to useful bi- or multifunctionalized oligomers. Forthcoming papers in this series will demonstrate that this is the case.[9]

Experimental Section

Experimental Procedure for the Polymerization of 2-Methylpropene at Room Temperature in the Presence of $TiCl_4$. Reactions were carried out in a closed thick-wall glass reactor allowing pressures higher than 1 bar. The solvent (methylene dichloride dried by distillation over phosphorus pentoxide, 200 cm^3) was introduced under nitrogen. After cooling to −20 °C, nitrogen was pumped off and 2-methylpropene was introduced by vacuum distillation. Then the mixture was allowed to warm to room temperature, and the catalyst (titanium tetrachloride) was introduced as a concentrated solution in methylene dichloride by a syringe through a rubber cap. After the required reaction duration, the polymerizing mixture was quenched by a small quantity of methanol containing 10% (vol ratio) aqueous ammonia.

Experimental Procedure for Polymerizations in the Presence of Diethylaluminum Chloride. Hydrazoic acid was prepared according to the usual procedure which has already been described.[10] It was obtained in the form of a solution in methylene dichloride. This solution was dried over phosphorus pentoxide and dosed before use.

Diethylaluminum chloride (Aldrich), solution 1 M in hexane, was used as provided by the supplier.

Methylene dichloride was distilled twice over phosphorus pentoxide, the second time being carried out directly under vacuum inside the polymerization equipment.

2-Methylpropene was used as provided by the supplier (Air Liquide).

The polymerizations were carried out in polymerization equipment under vacuum (10^{-4} Torr). The solvent was introduced first, followed by the solution of hydrazoic acid and then

2-methylpropene. When the mixture was at the required temperature (−50 °C in the present study), the solution of catalyst was introduced by a syringe through a rubber cap.

Acknowledgment. Paramins of Exxon Chemical is gratefully acknowledged for supporting this research.

References and Notes

(1) For part 4 of this series, see ref 10.
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(3) Permanent address: Paramins, Exxon Chemical Co., P.O. Box 536, Linden, NJ 07036.
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