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Synthesis of Polymers Containing Pseudohalide Groups by Cationic Polymerization. 9.[†] Azido End-Capped Poly(2-methylpropene) by Polymerization Initiated by the System Lewis Acid–2-Azido-2-phenylpropane

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ABSTRACT: The polymerization of 2-methylpropene in methylene dichloride can be initiated by 2-azido-2-phenylpropane (APP) in the presence of some Lewis acids. The system APP–boron trichloride gave only the usual polymer functionalization by a tertiary chloride at one chain end and the cumyl moiety at the other end. The system APP–antimony pentafluoride gave no significant functionalization. The system APP–titanium tetrachloride gave a polymer which was partly functionalized by an azide group. The system APP–boron trifluoride gave complete functionalization within experimental accuracy. These experiments show that, by cationic polymerization of 2-methylpropene and using the suitable initiator–Lewis acid combination, it is possible to obtain by direct synthesis from the monomer a polymer specificially functionalized by a carbon-to-nitrogen bond. Less specific functionalization is also possible in a nonpolar medium.

Introduction

This paper is the continuation of a series aiming at opening a field of new monomers, polymers, and copolymers containing functions of the pseudohalide type, using cationic polymerization.[1–6] The previous papers showed that it is possible to achieve the direct functionalization of poly(2-methylpropene) (PMP) by coinitiation with 2-azido-2,4,4-trimethylpentane with an acceptable azide functionality,[7a] with 2-isothiocyano-2,4,4-trimethylpentane,[7b] and with 2-isothiocyano-2-phenylpropane,[7c] these last two initiators producing PMP functionalized by an isothiocyanate and a thiocyanate group, depending on the conditions. This paper presents some results aiming at expanding the field of functionalization by coinitiation with 2-azido-2-phenylpropane (APP). It was expected that the higher mobility of its azide group would lead to easier functionalization, demonstrating the potential of this new chemistry.

Results and Discussion

Functionalization of PMP by Polymerization Initiated by APP Using Different Lewis Acids in Polar Medium. This study has been done in order to determine the functionalization efficiency of different APP–Lewis acid systems in the polymerization of 2-methylpropene. $TiCl_4$, BCl_3, BF_3, SbF_5, and $EtAlCl_2$ were selected for the present set of experiments. The monomer concentration was 1.12 M, the solvent was dichloromethane, and the temperature was −50 °C. Different runs are described in Table 1.

Table 1 shows that azide functionalization is obtained only with $TiCl_4$ and BF_3. In all cases, APP plays the role of initiator since all polymers contain aromatic nuclei. In the case of BF_3, the functionalization was apparently good since the functionality in both functions (azide group by infrared spectroscopy and SEC and aromatic nucleus by proton NMR spectroscopy and SEC) was equal to 1 within experimental accuracy.

In the case of SbF_5 the azide functionality was found to be negligible, but the phenyl ring functionality, according to the method described in the Experimental Section, was equal to 0.5. The general spectrum of this polymer is shown Figure 1. The methyl groups close to

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Table 1. 2-Methylpropene Polymerization Initiated by APP in the Presence of Different Lewis Acids (LA) in CH_2Cl_2 at -50 °C[a]

no.	APP, M	LA, M	LA/APP	yield, %	M_n, SEC	f_{Ph}	f_{N3}
1	0.05	$TiCl_4$, 0.05	1	100	1700	0.65	0.6
2	0.075	BCl_3, 0.08	1.06	80	1700	1.1	0
3	0.05	BF_3, 0.05	1	90	3700	1.15	1.2
4	0.032	SbF_5, 0.032	1	50	1200	0.5	0
5	0.024	$EtAlCl_2$, 0.045	1.9	95		0.4	0

[a] 2-Methylpropene concentration equal to 1.1 M. Polymerization time = 30 min.

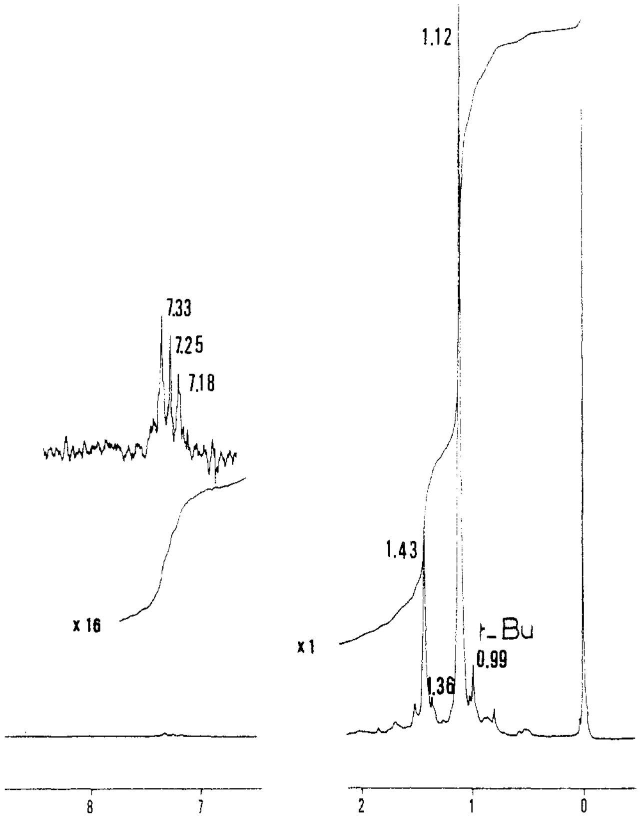

Figure 1. 100-MHz protonic spectrum of the polymer obtained by the initiation of 2-methylpropene polymerization by the APP–SbF_5 system at -50 °C in CH_2Cl_2.

the phenyl ring appear at around 1.36 ppm. The peak at 0.99 ppm corresponds to *tert*-butyl groups. The measurement of its intensity, relative to the intensity of the peak belonging to the repeat units, shows that about half of the macromolecules are initiated by the reaction between a proton and a 2-methylpropene molecule. The termination reaction is not known, since there is neither terminal unsaturation nor an azide group. Regardless, this system was not further investigated precisely because of this lack of functionalization.

The polymerization chemistry induced by the system APP–$EtAlCl_2$ seems to be different. No azide functionalization is obtained. The *tert*-butyl group content is witnessed by the presence of a small peak at 0.99 ppm, but its content is at the limit of the sensitivity of the spectroscopy used for this determination (100 MHz). The presence of a peak at 1.68 ppm indicates that a termination process is the formation of a tertiary chloride chain end. The complete absence of functionalization by an azide group shows that this system was not worthy of further investigation, as in the case of SbF_5. This set of experiments with various Lewis acids was carried out in order to allow a rationalization of the effect of Lewis acids. It can be seen that their influence is more complicated than expected. Consequently, it was decided to examine each acid in further details, or at least the Lewis acids which gave some hope of success in PMP functionalization. This will be the subject of this paper and further papers in this series. BCl_3 is only briefly investigated here for the sake of comparison with previous work.[8]

Table 2. Polymerization of MP (Concn = 1.1 M) Initiated by the BCl_3–APP System in CH_2Cl_2, Reaction Time of 30 min

	BCl_3, mol/L	APP, mol/L	yield, %	T, °C	M_n, SEC	f_{Ph}[a]
1	1.6×10^{-2}	10^{-2}	30	-50	1900	1.1
2	10^{-2}	10^{-2}	50	-50	1400	0.5
3	10^{-2}	10^{-2}	10	-80	3600	0.6
4	8×10^{-2}	7.5×10^{-2}	80	-50	1700	1.1

[a] Number of aromatic nuclei per macromolecule, determined by ^1H NMR spectroscopy and calculated from M_n, SEC.

Polymerization of 2-Methylpropene Initiated by BCl_3. This series of experiments has been performed within the same experimental conditions as above. Some characteristic results are shown in Table 2. Experiment 4 is the same as experiment 2 already described in Table 1.

Table 2 makes possible the following comments. The azide functionality of the macromolecules was always found to be equal to 0, according to the determination done by infrared spectroscopy. In the case of this BCl_3/APP system, the reaction yield decreased with decreasing temperature, as shown by the comparison of experiments 2 and 3. For these experiments, not all macromolecules are initiated from the APP molecule, as shown by the aromatic functionality which is largely lower than 1. Experiments 1 and 4 show that, at a ratio of initiator to Lewis acid higher than 1, it is possible to find conditions where initiation takes place from the APP molecule. While the number of runs quoted in Table 2 is not large enough to allow extensive discussion, it is clear that the phenyl group content is close to 1 per macromolecule when the Lewis acid is in excess. This observation may indicate that in order to achieve proper ionization and initiation, more than one molecule of Lewis acid is needed per azide group. This tentative assumption is consistent with the low yield found at low temperature, conditions which would favor complexation.

NMR spectroscopy shows that functionalization is achieved by termination by chlorination from the counteranion. It is clear that increasing APP concentration increases the polymerization yield. The ^1H NMR spectrum of the polymer corresponding to experiment 4 does not show any signal corresponding to terminal unsaturation (Figure 2) and indicates that the macromolecules are terminated by a tertiary chlorine atom corresponding to the peak at 1.68 ppm. The peak at 0.80 ppm seems to be due to an irregular structure, the nature of which is not totally understood at present. The peak at 1.37 ppm is assigned to the two methyl groups close to the phenyl ring, and the peak at 1.85 ppm is assigned to the CH_2 of the same group. The consequence of this analysis is that the phenyl rings incorporated in the polymer are "head groups" and do not belong to some poly(α-methylstyrene) units. These units could have been produced by APP dehydroazidation and subsequent copolymerization.

The possibility of indanic cyclization of the aromatic initiator is not mentioned here, although this is a well-known side reaction observed when using cumyl-type initiators for MP polymerization. The occurrence of this reaction can be demonstrated by analyzing the low molecular weight products extracted from the polymerization medium. It might be the case here, except for run

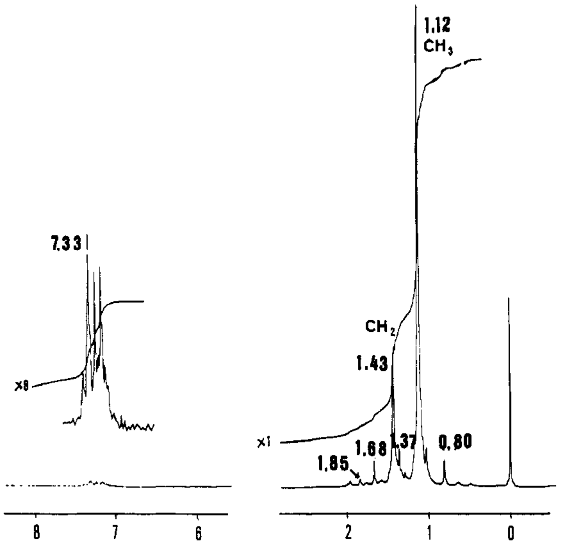

Figure 2. 100-MHz protonic spectrum of the polymer obtained by the initiation of 2-methylpropene polymerization by the APP–BCl_3 system at –50 °C in CH_2Cl_2.

Table 3. 2-Methylpropene Polymerization Initiated by APP in the Presence of Boron Trifluoride in CH_2Cl_2 at –50 °C, with a Reaction Time of 30 min

no.	APP, M	BF_3, M	IB, M	yield, %	M_n, SEC	f_{Ph}	f_{N3}
1	0.05	0.05	1.12	90	3700	1.15	1.2
2	0.03	0.03	0.23	80	1700	1.1	0.8
3	0.05	0.05	1.12	100	1300	0.8	0.5
4	0.031	0.062	1.12	100	1600	0.4	0.1
5	0.023	0.04	1.12	100	2900	0.5	0.1
6[a]	0.05	0.05	1.12	84	1200	0.4	0

[a] Experiment carried out at –20 °C.

1 (Table 2) where the number of phenyl rings contained in the polymer matches well the number of initial APP molecules. In other words, it could be suggested that an excess of Lewis acid is detrimental to the indanic cyclization process. Once again, the number of experiments carried out in this study do not allow us to draw definite conclusions on this particular point.

Polymerization of 2-Methylpropene Initiated by the BF_3–APP System. Polymerization in Methylene Dichloride. Some experiments were carried out in a polar medium (CH_2Cl_2) under various conditions and are described in Table 3. One experiment (2) has been done at –50 °C, the 2-methylpropene concentration being 2.3 × 10^{-1} M and the BF_3 and APP concentrations being around 3 × 10^{-2} M. The polymerization yield was 80%, and the molecular weight was 1700. The azide content, determined by infrared spectroscopy, gave a functionality equal to 0.8 (Figure 3). The aromatic nuclei functionality, determined by ^1H NMR spectroscopy and calculated from the average number molecular weight determined by SEC, was found to be equal to 1.1 (Figure 4).

This result can be very simply interpreted, assuming initiation through the complexation of APP by the Lewis acid followed by ionization. The fact that both functionalities in the aromatic nucleus and in the azide group were close to 1 for experiment 2 shows the specificity of the initiation and functionalization processes. However, it is to be noted that the polymerization yield is lower than 100%. This result suggests that functionalization is obtained through a termination process. A small peak at 0.99 ppm shows a trace of protonic macromolecular chain initiation. This event is probably due to cocatalysis. No unsaturation was found, demonstrating the absence of proton transfer to any detectable amount.

SEC analysis of the polymer (Table 3, no. 2) (with double detection UV and RI) was carried out, showing that a small fraction of the polymer (around 8% in weight) is not functionalized by the aromatic nucleus. These molecules could be assigned to cocatalysis, according to the fact that the azide functionality is slightly lower than 1. Cocatalysis is known to be very effective with this Lewis acid, and this fact supports the conclusion that the molecules bearing no aromatic nucleus are initiated by cocatalysis. It is worth noting that the sensitivity of the proton NMR spectroscopy used in this study (100 MHz) does not allow the determination of the unsaturation content when this content is too low.

The most important result is certainly the fact that a nearly perfect bifunctionality has been obtained with the combination 2-azido-2-phenylpropane/boron trifluoride when these materials are used in a one-to-one stoichiometry, one macromolecular end being functionalized by an aromatic nucleus, the other by an azide group.

The other experiments carried out using the APP/BF_3-initiating system shown in Table 3 deserve some comments. They were carried out at higher monomer concentration. The azide content is determined by IR spectroscopy, and the aromatic nuclei content is determined by ^1H NMR spectroscopy. The functionalities in aromatic nuclei f_{Ph}, and in azide group f_{N3}, have been calculated using the SEC molecular weight determination. In the case of experiment 3, the oligomers contain a high molecular weight fraction as observed by SEC. See peak A in Figure 5 which displays a chromatogram with double detection (UV and RI) of the polymer obtained in run 3.

The influence of the polymerization temperature must be discussed. It is obvious from these experiments and from others not quoted in Table 3 that the functionality in azide function f_{N3} is equal or nearly equal to the aromatic nucleus functionality f_{Ph} only at a temperature equal or lower than –50 °C. It is also clear that the lowest values for f_{Ph} are obtained in conditions corresponding to the lowest values of the APP concentration. Another observation is that the polymerization yield, calculated on the total amount APP + 2-methylpropene, is sometimes lower than 100%. This result seems to rule out the possibility of a living system, at least in the conditions of the present experiments. Experiment 1 gives a polymerization yield of 90%. Taking into account the functionality, this yield corresponds to a 2-methylpropene consumption of around 97%, which is considered to be a complete consumption within experimental errors. Thus, this experiment seems to demonstrate that it is possible to find conditions in which a nearly complete functionalization with a high conversion of the monomer is observed. SEC chromatograms of the polymers of experiments 1 and 3 (Table 3) are similar to the one presented in Figure 5 and show that the polymers contain a small proportion of a high molecular weight fraction. Detection by UV absorption shows that this fraction is not functionalized. It is worth recalling here that cocatalysis by water has a tendancy to produce high molecular weight polymers. Consequently, as above, it is assumed that this fraction is due to the presence of residual moisture. This assumption is in agreement with the irreproducibility of the functionalization and molecular weight, the moisture level varying randomly. The comparison of the experimental molecular weight, determined by SEC, and the theoretical molecular weight, assuming that each APP molecule gives a macromolecule, shows only a rough agreement. At constant temperature, the highest functionality value is obtained for the highest concentration of APP.

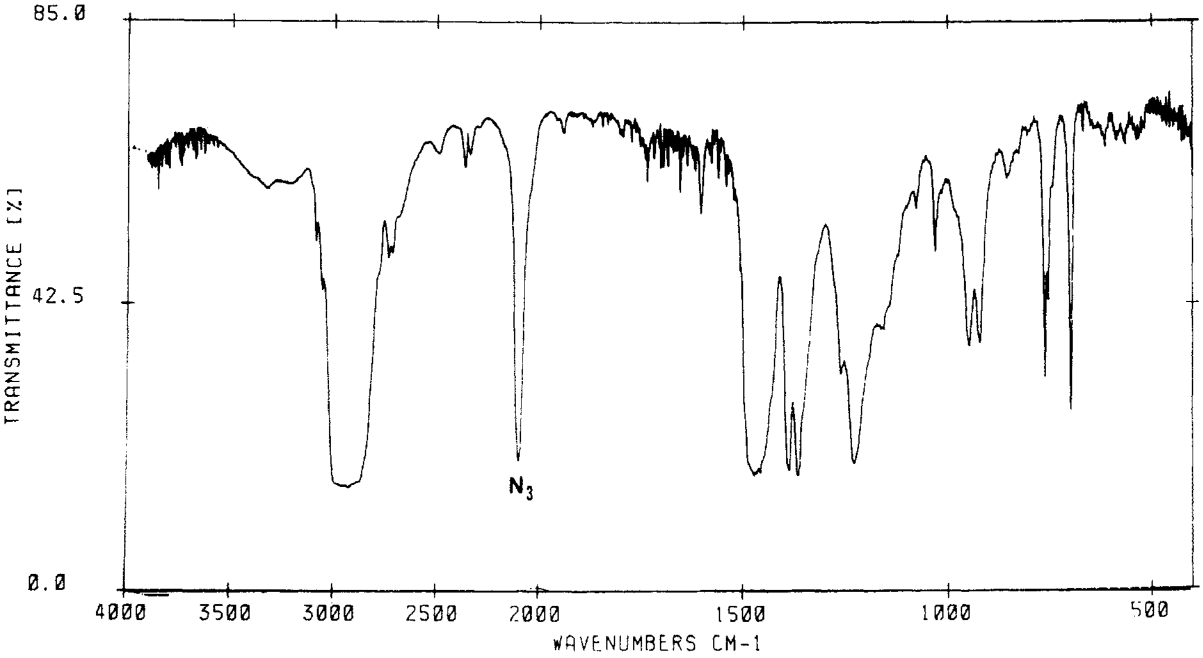

Figure 3. Infrared spectrum of the poly(2-methylpropene) obtained by initiating the polymerization by the APP–BF_3 system at −50 °C in CH_2Cl_2, experiment 2, Table 3.

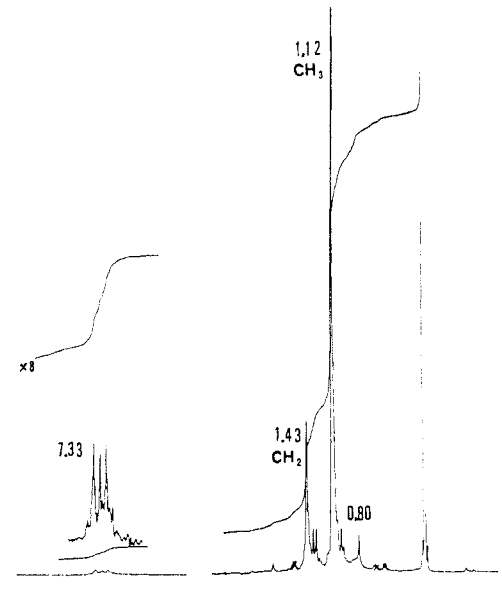

Figure 4. 100-MHz protonic spectrum of the polymer obtained by the initiation of 2-methylpropene polymerization by the APP-BF_3 system at −50 °C in CH_2Cl_2, experiment 2, Table 3.

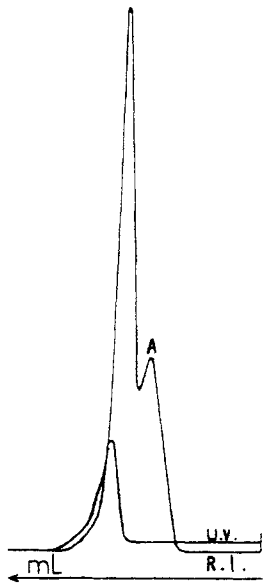

Figure 5. SEC chromatogram with double detection—UV and refractive index (RI)—of polymer obtained initiating the polymerization by the APP–BF_3 system at −50 °C in CH_2Cl_2, experiment 3, Table 3.

It is possible to distinguish between initiation with the APP/BF_3 system and a possible cocatalysis by HN_3 which could be produced by dehydroazidation of APP induced by the presence of BF_3. If the interactions between the initiator and the Lewis acid would produce dehydroazidation of the organic azide initiator, the aromatic ring content would be due to the copolymerization of 2-methylpropene with α-methylstyrene. However, the structure of the carbon α to the phenyl ring produced by this copolymerization would be different from the same carbon corresponding to coinitiation

PIB-CH_2-$C(C_6H_5)(CH_3)$-PIB and C_6H_5-$C(CH_3)_2$-PIB

respectively. In the last structure, as described in the Experimental Section, the two methyl groups attached to the α carbon give a peak on proton NMR spectrum at 1.36 ppm in $CDCl_3$. The spectrum of the polymer corresponding to experiment 3, Table 3, shows the peak at 1.33 ppm of the two methyl groups corresponding to the terminal tertiary azide, the peak at 1.36 ppm assigned to the two methyl groups close to the terminal benzene ring, and the peak at 1.85 ppm assigned to the methylene closest to the same benzene ring. There are also some unsaturated chain ends.

This result shows that if there is initiation from APP, there is also a side reaction which prevents the complete fixation of the azide group at the end of the macromolecules. Indeed, it is worth noting that transfer reactions, when they are present, should not prevent the same functionality in azide functions and in the aromatic nuclei from being obtained. In other words, these exploratory experiments show that there is a dehydroazidation reaction which takes place identically on active centers present in the systems containing either APP or HN_3 in the presence of BF_3. To support this conclusion, an experiment has been carried out in the following conditions: MP = 1.12 M, HN_3 = 0.032 M, BF_3 = 0.016 M at −50 °C in methylene

Table 4. 2-Methylpropene Polymerization Initiated by the BF_3/APP System in Hexane at -50 °C[a]

no.	APP, M	BF_3, M	IB, M	M_n, GPC	M_nth[b]
1	0.037	0.046	1.125	1500	1860
2	0.046	0.046	2.25	1900	2900
3	0.05	0.05	3.375	1900	3940

[a] Reaction duration, 50 min. [b] The theoretical M_n is calculated from the ratio of the initial concentration of monomer to APP.

dichloride. The yield was 100% with an average number molecular weight of 1600. The azide functionality was only 0.2, before and after cleaning of the oligomers.[9] This value is of the same order of magnitude as that obtained with APP in similar conditions.

Experiment 6 (Table 3), carried out at around -20 °C, gives an azide functionality equal to 0. This finding means that there is no possible azide functionalization by polymerization in the presence of BF_3 at a temperature higher than ca. -30 °C in polar medium. This conclusion means that BF_3 is not the best choice among Lewis acids to obtain functionalization by polymerization, due to too strong interactions with the azide group.

The conditions to achieve the best PIB functionalization by polymerization using the BF_3/APP system are summarized below. It is desirable to work at a temperature equal or lower than -60 °C and at a relatively high APP concentration (0.05 M or higher) to minimize the effect of cocatalysis and at a ratio BF_3/APP close to 1, while this last point does not seem to be very critical. Our study pointed out that there is probably a dehydroazidation reaction taking place on the azide function in the presence of BF_3.

Polymerization in Hexane. According to the above results, it was of interest to investigate the effect of the medium polarity. Three different typical runs are described in Table 4. In all cases the temperature was -50 °C and the initiator concentration was around 0.05 M. Complete conversion was always obtained. The major difference between the three experiments lies in the procedure of monomer introduction. For the first one (experiment 1), the monomer was introduced in one shot before the introduction of the initiator. For the second (experiment 2), a second monomer charge, identical to the first one, was introduced after the polymerization of the first was over. For the third experiment (experiment 3), this operation was repeated once more. Thus, monomer concentration is quoted in Table 3 for experiment 2 as twice that of experiment 1 and for experiment 3 as three times that of experiment 1. The theoretical average number molecular weight is calculated with the total monomer charge, all the coinitiator molecules being used. It is clear that the system does not seem to possess any living character, at least to a reasonable extent, since monomer addition does not induce an equivalent increase of the molecular weight, although polymerization yields were complete.

Detailed analyses were carried out on the products of these experiments. It was shown by SEC that the distributions of the molecular weights were quasimonomodal. Figure 6 shows the SEC chromatogram of the three polymers. The polydispersity index is high, around 4, which is an indication that the actual low propagation rate could be faster than initiation rate.

The results of various analyses are reported in Table 5. The comparison between the determinations of the azide group content by infrared and ^1H NMR spectroscopy (second and seventh columns, Table 5) are in reasonable agreement, while the NMR determination gave a systematically higher value, probably due to some steric impurity giving resonance at the same chemical shift of 1.33 ppm. The aliphatic range for polymers no. 1 is shown in Figure 7. The NMR spectrum of the unsaturated region of this polymer (Figure 8) shows that terminal unsaturations are present. Figure 7 shows the usual *tert*-butyl group appearing at 0.99 ppm, the methyl group close to the azide group at 1.33 ppm, the methylene group close to the azide group at 1.59 ppm, and the methylene group close to the aromatic ring at 1.85 ppm. Figure 8 shows that the usual two types of terminal unsaturations are present. The peak at 5.15 ppm corresponding to the trisubstituted terminal unsaturations shows that this structure content is about half that of the disubstituted unsaturations (4.64 and 4.84 ppm). The aromatic resonance shows a complicated pattern which suggests that different types of aromatic nuclei may coexist in the polymer. This is confirmed by the fact that the peak at 1.85 ppm, assigned to the methylene group close to the aromatic nuclei of a cumyl-type structure, does not appear in the 2/5 ratio as expected. These various aromatic structures could correspond, besides the phenyl ring head group, to phenyl ring side groups due to the dehydroazidation of the initiator and further copolymerization of α-methylstyrene. They could also be produced by alkylation of the initial head group. However, it is worth mentioning that alkylation was not noticed, polymerizing in CH_2Cl_2, at least to a measurable extent. This point will certainly deserve attention in the future.

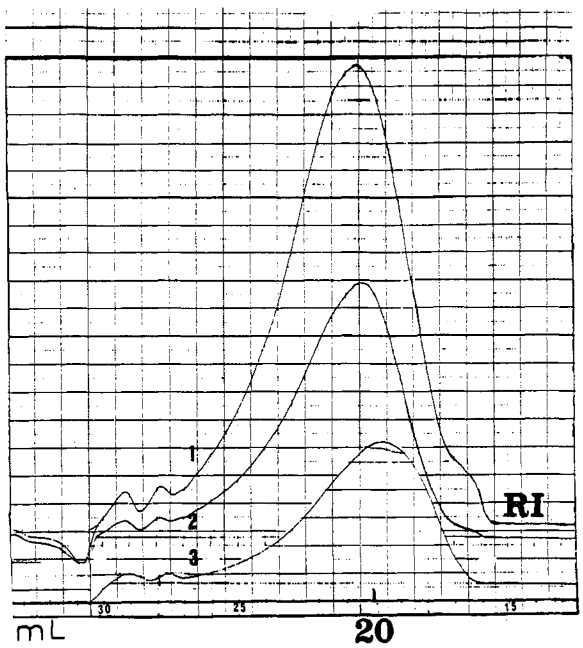

Figure 6. SEC chromatogram (RI detection) of polymers corresponding to experiments 1, 2, and 3, Table 4, in nonpolar medium using the APP-BF_3 system at -50 °C.

Table 5. Characteristics of 2-Methylpropene Oligomers Obtained in Nonpolar Medium (APP/BF_3 System) at -50 °C[a]

expt	X (IR)	X_{Ph}	X_{tBu}	$X_{ins.1}$	$X_{ins.2}$	X_{N3}
1	3.1	2.2	5.1	1.6	0.7	2.8
2	2.0	1.8	6.3	3.3	2.0	2.1
3	1.8	1.4	7.7	4.1	0.9	2.0

[a] All the function contents are expressed in 10^{-4} mol/g of polymer units. X (IR) is the azide content determined by infrared spectroscopy; X_{Ph}, X_{tBu}, $X_{ins.1}$, $X_{ins.2}$, and X_{N3} are, respectively, the phenyl ring, the *tert*-butyl group, the terminal disubstituted double bonds, the terminal trisubstituted double bonds, and the azide group contents determined by ^1H NMR spectroscopy.

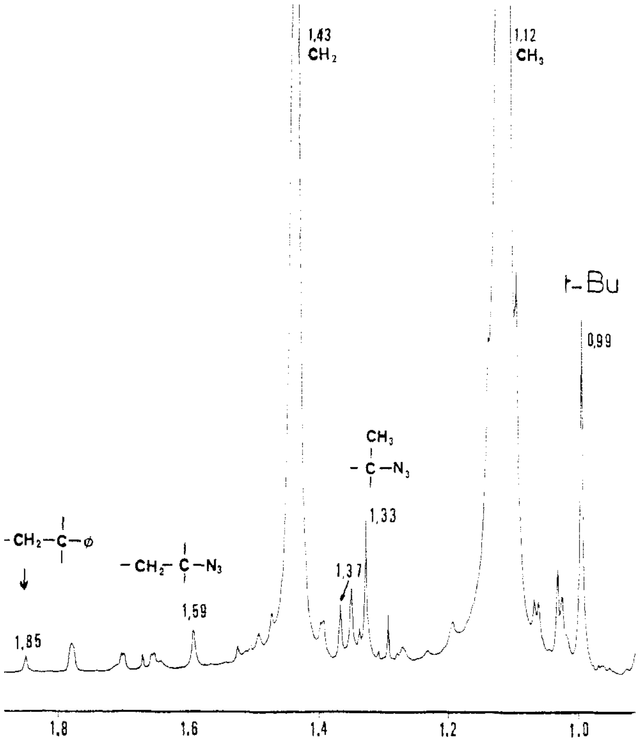

Figure 7. 300-MHz spectrum of the aliphatic range of protonic resonance for polymer 1, Table 4.

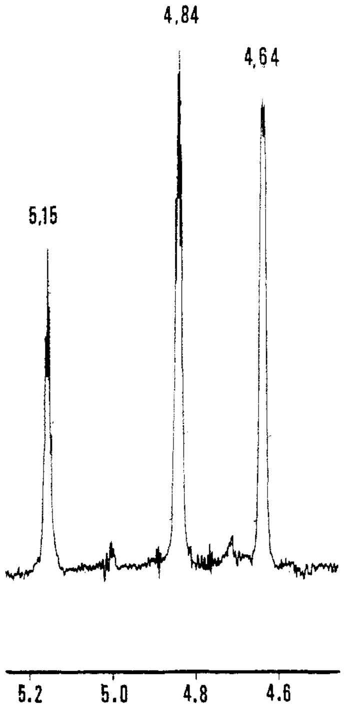

Figure 8. 300-MHz spectrum of the unsaturated range of protonic resonance for polymer 1, Table 4.

The *tert*-butyl group content of the polymers increases from sample 1 to sample 3. A rough measure of the initiator activity is given by the aromatic nucleus content compared to the number of oligomer molecules. We found, respectively, for experiments 1, 2, and 3 that 42%, 40%, and 38% of the oligomers were functionalized by an aromatic nucleus. This slight decrease of the relative aromatic content is evidently due to the increasing importance of transfer. As for the overall efficiency of the APP initiator, we can calculate that the proportions of APP molecules used in the three types of experiments were, respectively, 39%, 53%, and 54%. A first explanation of this result is that initiation on APP did take place on unreacted APP when the second monomer charge was added to the polymerizing medium and is in tune with the previous assumption that initiation rate is low compared to the propagation rate. A second explanation is that dehydroazidation produced α-methylstyrene, which copolymerized further with isobutylene. The complicated pattern obtained for the aromatic resonance, and mentioned above, indicates that both explanations are relevant to the present phenomenology.

If we take for azide group content the average of the IR and NMR determinations, the ratio of the aromatic nuclei to azide group contents can be calculated, and for experiments 1, 2, and 3 are found, respectively, to be equal to 0.74, 0.88, and 0.74. These results show that the number of aromatic nuclei is always lower than that of azide group. This finding is explained by the dehydroazidation of the initiator (APP) which generates "in situ" hydrazoic acid which participates in polymerization initiation by cocatalysis. Consequently, not only azide groups produced by initiation by APP but also azide groups produced by cocatalysis with HN_3 must be found in the final polymer.

The determination of the *tert*-butyl group content confirms the above conclusion in the sense that this saturated end group is found even in polymer 1, Table 4, which shows the importance of transfer and dehydroazidation of the initiator even with the "classical" procedure, i.e., when the monomer is introduced before the initiator.

Quantitative analysis of the NMR spectra of polymers 1, 2, and 3 shows that this relative unsaturation content of the polymers is increasing from polymer 1 to polymer 3. This is in tune with the fact that the relative importance of the azide group is decreasing from polymer 1 to polymer 3. Transfer and dehydroazidation reactions explain why the polymerization yield is complete.

Conclusion

To summarize our observations, in polar medium it seems possible to synthesize azido end-capped poly(2-methylpropene) using the APP–BF_3 system. This functionalization is achieved by an "Initer" rather than by an "Inifer" mechanism. For some reasons which are not completely clear, cocatalysis by water seems to be markedly reduced when the ratio of initiator to Lewis acid is close to unity. Another important characteristic is that proton transfer is substantially reduced. It can be suggested that complexation of the Lewis acid by the initiator is a fast reaction in polar medium.

Our work points to the fact that functionalization in nonpolar medium is possible using the APP–BF_3 system, but the specificity is severely decreased. It can be suggested that contact ion pairs, which are probably the major active species in nonpolar medium, favor proton extraction from the organic moiety of the active species, giving proton transfer. This point will deserve some particular study in the future.

Experimental Section

Hexane and CH_2Cl_2 were distilled over P_2O_5 and then stored under nitrogen before use.

BF_3 was used as such. It was handled under pressure in a closed system connected to a pressure bottle of known volume which was previously dried. A mercury manometer was used to measure the pressure, and the gaseous Lewis acid was allowed to penetrate in the polymerization vessel through a vacuum stainless steel stopcock in order to initiate the reaction. This procedure is certainly at the origin of a systematic error on the Lewis acid concentration, the actual concentration being less than the calculated one. However, from the residual pressure

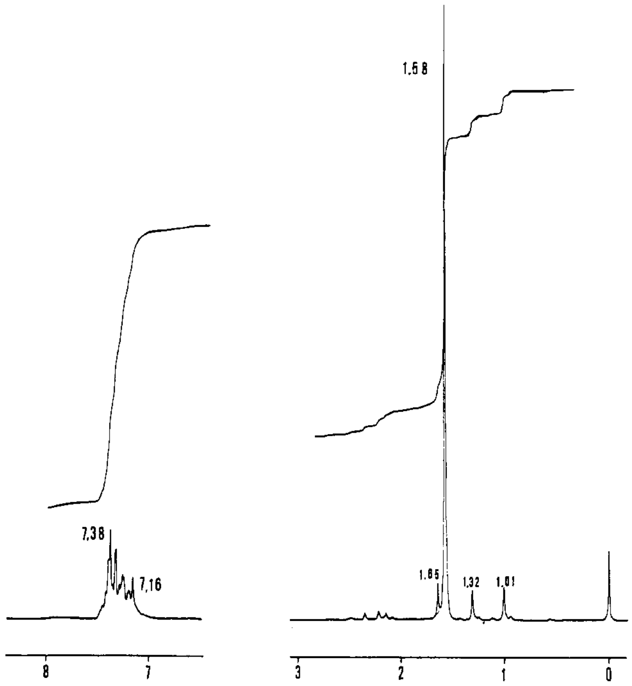

Figure 9. 100-MHz protonic spectrum of APP in CH_2Cl_2.

measured in the pressure bottle, it was estimated that this systematic error was less than 10%.

APP was synthesized according to a procedure previously described for the synthesis of 2-azido-2,4,4-trimethylpentane, by addition reaction of hydrazoic acid on α-methyl styrene in CH_2Cl_2 Part 3 of the present series of papers.[6] Its protonic NMR spectrum is shown in Figure 9. Small peaks at 1.01, 1.32, and 1.65 ppm are due to impurities. It was then purified by chromatography over silica gel (400 mesh) with CH_2Cl_2 as solvent. Its purity determined by vapor pressure chromatography was of the order of 95%.

2-Methylpropene was used as supplied by Air Liquide Company.

Polymerization Procedure. The polymerization procedure in the case of boron trifluoride is identical to the one used in the case of boron trichloride. The quantity of Lewis acid is determined volumetrically.

The previously described procedure for polymerization was employed without major change.[6] The following mixing sequenced was used: solvent (hexane or methylene dichloride), APP, 2-methylpropene, and boron trifluoride. The polymerization reactions were sometimes followed by recording the temperature so as to obtain an indication of the end of reaction. Polymerization of the monomer charge was obtained in less than 30 min. After quenching with 10 mL of a 10% (volume ratio) solution of aqueous ammonia in methanol, the polymer solution was filtrated and concentrated. The isolated polymer was analyzed by SEC, IR, and ^1H NMR spectroscopy.

The SEC analysis was carried out on microstyragel columns (100, 500, and 10^4 Å) at a THF output of 1 mL mn^{-1}.

^{1}H NMR Spectroscopy of Polymers. Proton analysis of the polymers was carried out at 100 MHz or 300 MHz in CD_2Cl_2 to allow the aromatic content determination. The peak at 1.37 ppm is assigned to the two methyl groups (A) close to the phenyl ring of the structure:

$$\underset{\text{(A)}}{C_6H_5\text{-}C(CH_3)_2}\text{-}\underset{\text{(B)}}{CH_2}\text{-}C(CH_3)_2\text{-PMP}$$

Using Harris's technique,[10] it was shown that these protons are borne by a carbon resonating at 31.3 ppm in the ^{13}C spectrum. It was confirmed that this small peak at 31.3 ppm is a methyl group by a DEPT experiment. This assignment is in agreement with the fact that the methyl resonance of the *tert*-butyl group of the 4-*tert*-butyltoluene appears at 1.30 ppm.[11] Similarly, the peak at 1.85 ppm, the surface of which is three times less than that of the peak at 1.37 ppm, is assigned to the CH_2 (B) of the same group.

Determination of the Azide Functionality by Infrared Spectroscopy. This method has been described in previous papers.[5] It is assumed hereby that the absorption coefficient of the azide group remains approximately constant when the organic moiety is changed, for instance, from aliphatic to aromatic. This assumption has been checked with a mixture of PMP and (azidomethyl)styrene. For instance, 9.5 g of PMP have been dissolved in 20 mL of dichloromethane. Then 0.779 g of (azidomethyl)styrene are introduced. After mixing, the mixture is vacuum dried and the spectrum is recorded. The weight fraction of the azide group is given by the above composition. Using the known absorption coefficient for aliphatic azides, the composition of the mixture and the theoretical weight fraction, are calculated. The fair agreement between these two values lends support to the assumption underlying this determination.

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