

**THE MASSACHUSETTS
TOXICS USE REDUCTION INSTITUTE**

**SOLVENT REDUCTION
TECHNOLOGIES:
MACROMERIC SURFACTANTS IN
EMULSION POLYMERIZATION**

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Solvent Reduction Technologies:

Macromeric Surfactants in Emulsion Polymerization

Savvas Hadjikyriacou
Ph.D Candidate, Polymer Science

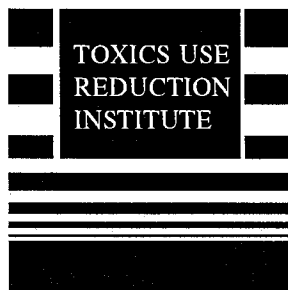
Professor Rudolf Faust
Department of Chemistry

University of Massachusetts Lowell

The Toxics Use Reduction Institute Research Fellows Program

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Toxics Use Reduction Institute Research Fellows Program

In 1991 the Toxics Use Reduction Institute established the Research Fellows Program at the University of Massachusetts Lowell (UML). The Research Fellows Program funds toxics use reduction research projects performed by graduate students and their advisors. The goals of the program are:

- to develop technologies, materials, processes and methods for implementing toxics use reduction techniques,
- to develop an understanding of toxics use reduction among UML graduate students and faculty,
- to facilitate the integration of the concept of toxics use reduction into UML research projects, and
- to provide UML faculty with "incubator" funding for toxics use reduction related research.

The types of projects funded through the Research Fellows Program are technology, methods and policy research projects. Each final report is published by the Institute. The opinions and conclusions expressed in this report are those of the authors and not necessarily those of the Toxics Use Reduction Institute.

INTRODUCTION

During the period covered by the first and second progress reports (September-November 1992 and December-March 1993) a series of experiments have been carried out to investigate the ability of the tertiary butyl cation (2,2,4-trimethyl-4-chloro pentane (TMPCl) and chlorine terminated polyisobutylene (PIBCl)) to initiate the polymerization of silyl vinyl ethers (trimethyl vinyloxy silane and t-butyl dimethyl vinyloxy silane) using titanium tetrachloride (TiCl_4), titanium tetrabutoxide ($\text{Ti}(\text{OBu})_4$) and zinc chloride (ZnCl_2) as cointiators.

ZnCl_2 was not able to cointiate the polymerization of the silyl vinyl ethers using TMPCl or the PIBCl as initiators because of it is a weak Lewis acid. On the other hand TiCl_4 gave polymers with narrow molecular weight distribution ($\text{MWD}=1.2-1.3$) but rather low monomer conversions. These results can be explained by the strong nature of TiCl_4 as a Lewis acid, taking part in side reactions. In order to avoid these cointiator depleting side reactions the Lewis acidity of TiCl_4 was reduced by reacting it with $\text{Ti}(\text{OBu})_4$ in the ratio of 3:1 equivalents to form $\text{TiCl}_3(\text{OBu})$ which is milder than TiCl_4 . With this milder cointiator however we were not able to initiate the polymerization of the silyl vinyl ethers from TMPCl or to cross over from isobutylene polymerization to silyl vinyl ethers polymerization (PIBCl).

The polarity of the solvent system was also studied using the methyl chloride-hexanes (40-60%v/v) and pure methyl chloride systems. The use of the lower polarity solvent system (methyl chloride-hexanes) results in lower yields relative to the more polar methyl chloride though the molecular weight distribution is broad and bimodal in both cases. Bimodality may be due to direct initiation by TiCl_4 taking place parallel to controlled initiation.

To effect the polymerization of isobutylene and the efficient cross over reaction to silyl vinyl ethers polymerization we have also used the TiCl_4 - ZnCl_2 combination as cointiators. First isobutylene was polymerized in the presence of TiCl_4 followed by ethyl acetate or pyridine addition to quench TiCl_4 then ZnCl_2 was introduced to the reaction system and silyl vinyl ether was added last.

Both systems, TiCl_4 /ethyl acetate and TiCl_4 /pyridine give direct initiation and broad molecular weight distributions when they are used alone, but in the presence of ZnCl_2 narrow molecular weight distributions and close to theoretical molecular weights are obtained

The yields however remain low. This is attributed to low initiation efficiency of the system.

From the results of the above experiments we concluded that the t-butyl cation is an ineffective initiator for silyl vinyl ether polymerization and it is not suitable to yield close to 100% cross over reaction. The propagating cation is not stabilized and thus gives side reactions. Another group that is able to stabilize the propagating cation efficiently to give close to 100% cross over reaction is the diphenyl cation. The structure of the propagating cation with the two phenyl rings is planar and the two phenyl rings can resonance stabilize the cation and resulting in the efficient cross-over reaction. Diphenyl compounds are also excellent initiators for aldol group transfer polymerization¹.

The diphenyl cation can be introduced in the polymer structure by adding diphenyl ethylene to the polymerization system after the isobutylene conversion is complete. When the reaction is quenched with methanol a methoxy group is developed at the end of the polymer chain. This enables us to effect the initiation of the polymerization and the efficient cross over reaction from isobutylene polymerization to silyl vinyl ethers polymerization.

The cross over reaction is the most critical step in the process because to control the molecular structure and the molecular weights and distributions we have to achieve close to 100% cross over reaction. For this purpose our work has been concentrated on the capping reaction of polyisobutylene with diphenyl ethylene. In order to find reaction conditions for 100% capping reaction model compounds have been synthesized. The model compounds prepared have molecular structure close to that of the polymers. Model compounds synthesized include the following
1: t-butyl diphenyl chloro methane and 2: 1-methoxy-1,1-diphenyl ethane.

EXPERIMENTAL PART

Polymerization reactions were carried out in large culture tubes in a glove box under nitrogen atmosphere.

The solvents were purified and dried before use. Hexane was refluxed for 24 hours over sulphuric acid and washed three times with water to remove traces of acid. After being dried over Na_2SO_4 for at least 24 hours it was refluxed overnight over calcium hydride (CaH_2) and freshly distilled before used.

Methyl chloride was dried by passing it through columns of Drierite and barium oxide.

Lewis acids: titanium tetrachloride (TiCl_4), titanium tetrabutoxide ($\text{Ti}(\text{OBu})_4$), zinc chloride (ZnCl_2), boron trichloride (BCl_3) 1,1-diphenyl ethylene and 2,6-ditertiary butyl pyridine were used as received.

2,2,4-trimethyl pentyl chloride was prepared by chlorination of 2,2,4-trimethyl-1-pentene and purified by vacuum distillation.

Tertiary butyl dimethyl vinyloxy silane was synthesized in our laboratory².

t-butyl-diphenyl chloro methane was synthesized by the Grignard reaction of pivaloyl chloride with phenyl magnesium bromide. The hydrolysis gave the corresponding alcohol which by chlorinated by thionyl chloride to give t-butyl-diphenyl chloro methane.

1-methoxy-1,1-diphenyl ethane was synthesized from the reaction of methyl-diphenyl carbinol with sodium to form the corresponding alkoxide. Upon the addition of methyl iodide the methoxy diphenyl ethane is formed.

A typical experimental procedure for the capping of Polyisobutylene polymer with diphenyl ethylene is described below:

<u>REAGENT</u>	<u>CONCENTRATION</u>
1: MeCl / hexanes 40/60 ^{v/v}	-----
2: ditertiary-butylpyridine	0.005 M
3: TMPCl	0.020 M
4: isobutylene	0.360 M
5: TiCl_4	0.080 M
6: diphenyl ethylene	0.021 M

Polymerization reaction time 30 min

Capping reaction time 60 min

Polymerization temperature -80°C

Capping reaction temperature -80°C

The reagents were added to the reaction flask in the order mentioned above. The reaction at the end was quenched with methanol and the polymer isolated by pouring the reaction mixture into 10% ammoniacal solution in methanol. The organic phase (hexane-MeCl) separated and washed with water until neutral, dried over Na_2SO_4 overnight and the polymer was obtained by evaporating the solvent.

All polymers prepared were characterized by GPC and ^1H NMR.

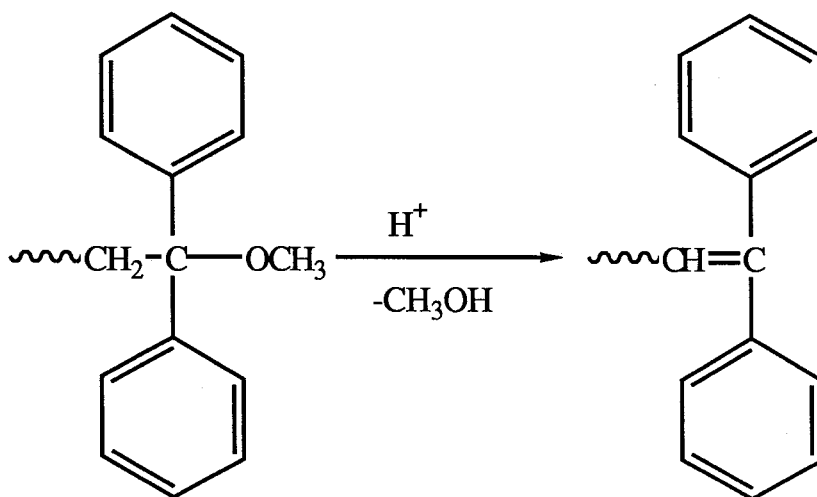
RESULTS AND DISCUSSION

The polymerization reactions of isobutylene were smooth and gave the expected molecular weights and narrow molecular weight distributions. The reaction conditions were more critical for the capping reaction than the polymerization.

Boron trichloride (BCl_3) was used initially to effect the capping of polyisobutylene with diphenyl ethylene but the results were poor because of the weak nature of BCl_3 as a Lewis acid. The reaction was unacceptably slow as it was indicated by ^1H NMR studies of the product of the reaction. Diphenyl ethylene was used in 10% excess relative to the PIB concentration and from calculations based on the ^1H NMR spectrum it was concluded that after four hours reaction time the reaction has proceeded only to 40%.

The capping reaction was carried out using TiCl_4 instead and initial results were most encouraging. The reaction of diphenyl ethylene with the chlorine terminated PIB was almost quantitative as it was indicated by ^1H NMR studies (Fig.1).

The reaction conditions critically affect the results. The presence of acids in the reaction mixture catalyzes the elimination of methanol (dealcoholation) from the end of the polymer chain and the formation of unsaturation.



The unsaturation at the end group of the polymer chain is undesired because it cannot initiate the polymerization of the silyl vinyl ethers as can be done by the methoxy group in combination

with the presence of a Lewis acid. Quenching the capping reaction with pure methanol produces hydrogen chloride by the reaction between TiCl_4 and MeOH that catalyzes the elimination and the formation of unsaturation (Fig.2). The use of a 10% ammoniacal solution in methanol instead neutralizes the formed hydrogen chloride by forming ammonium chloride (NH_4Cl) and prevents decomposition and the formation of the unsaturation.

The reaction time and the concentrations of the reactants are also critical for successful capping reaction. The capping reaction has been found to require approximately one hour to approach completion and slight excess (5-10%) of diphenyl ethylene.

The concentration of the TiCl_4 is also critical in the capping reaction the best found to be close to four times the concentration of the initiator or the diphenyl ethylene. The use of large excess of TiCl_4 (16 times the initiator's concentration) leads to broad molecular weight distribution.

Figure 1 shows the ^1H NMR of the product of a capping reaction. Quenching was done using a 10% ammoniacal solution in methanol. At 5.3 ppm we observe the peak due to the double bond of the unreacted diphenyl ethylene and as it has been mentioned before it corresponds to a slight amount of unreacted diphenyl ethylene. The peak at 3.0 ppm is assigned to the protons of the methoxy group at the end of the polymer chain. The presence of the aromatic protons is indicated between 7 and 7.5 ppm. Presence of unsaturation is not indicated by the ^1H NMR.

In Figure 2 the ^1H NMR spectrum of the product of a capping reaction which was quenched with pure methanol can be seen. Here we do not observe the protons due to the methoxy group but instead we observe the presence of methanolic protons (peak at 3.5 ppm) and the unsaturation approximately at 6.0 ppm.

CONCLUSION

Functional PIB carrying methoxy endgroups has been developed. The polymer prepared carrying diphenyl alkyl methyl ether at the end of the chain can be used to initiate the polymerization of silyl vinyl ethers in the presence of a Lewis acid and give block copolymers with controlled molecular weight and structure.

FUTURE WORK

Our interest is concentrated on the formation of PIB-b-(t-butyl dimethyl vinyloxy silane) block copolymers which by using the functional initiator 3,3,5-trimethyl-5-chloro-1-hexyl methacrylate can be converted to functional block copolymers. The macromeric surfactant arises by hydrolysis of the siloxy groups and the formation of hydroxy groups under acidic conditions. The presence of the double bond on the block copolymer enables the macromeric surfactant to be polymerized while the presence of the hydroxyl groups offer the hydrophilicity which can be balanced by the hydrophobic block of the macromeric surfactant by controlling the molecular weights of the the hydrophobic and the hydrophilic blocks.

After its preparation and characterization the macromeric surfactant will be tested in emulsion polymerization by copolymerization with other monomers such as vinyl acetate, methyl methacrylate or styrene. It's copolymerization behavior will be observed. The properties of the latices and polymers prepared will also be studied and compared to other polymers prepared by conventional emulsifiers (surfactants).

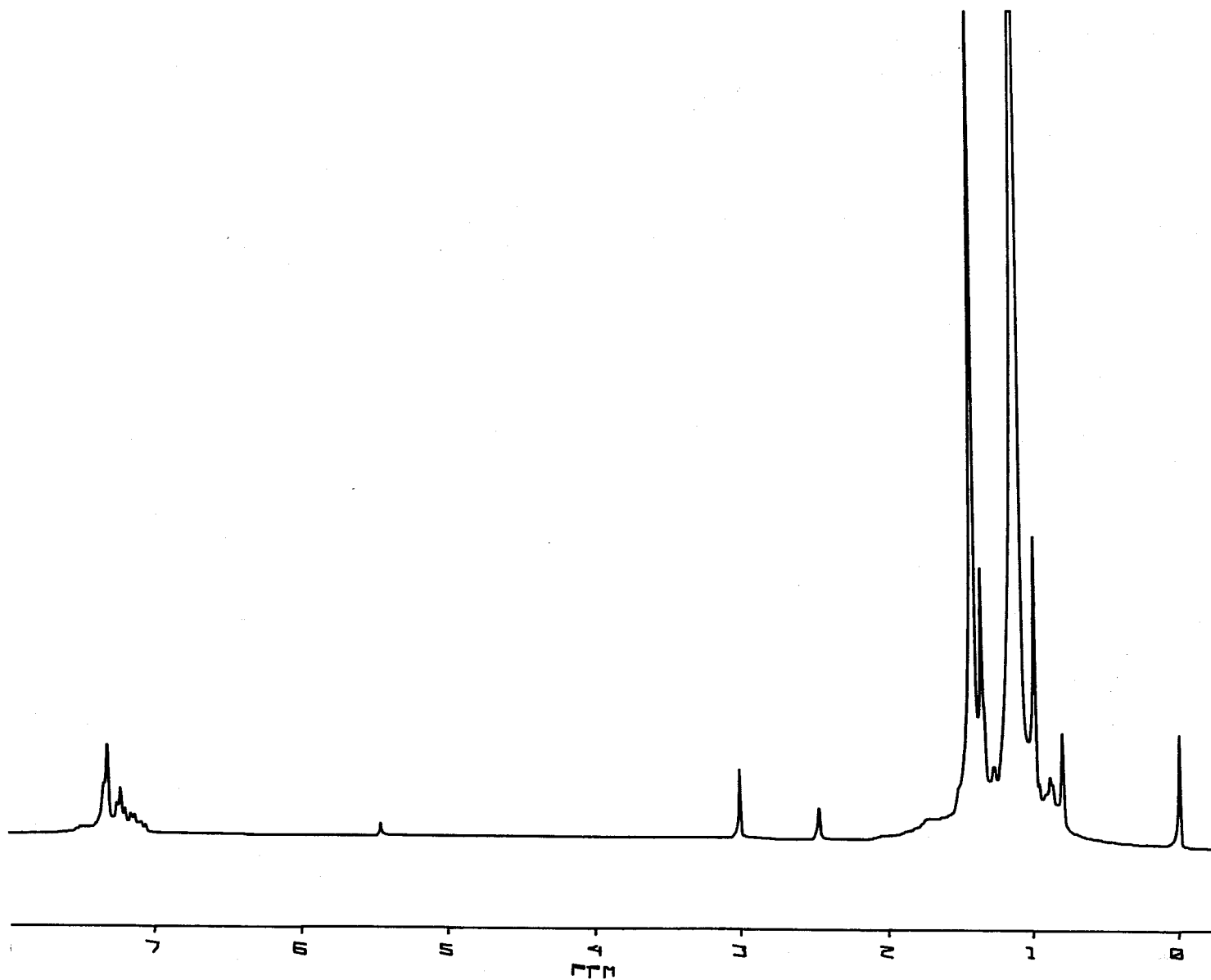


Figure 1: The ^1H NMR spectrum of PIB-DPE capped. The reaction was quenched with 10% v/v ammoniacal solution in methanol.

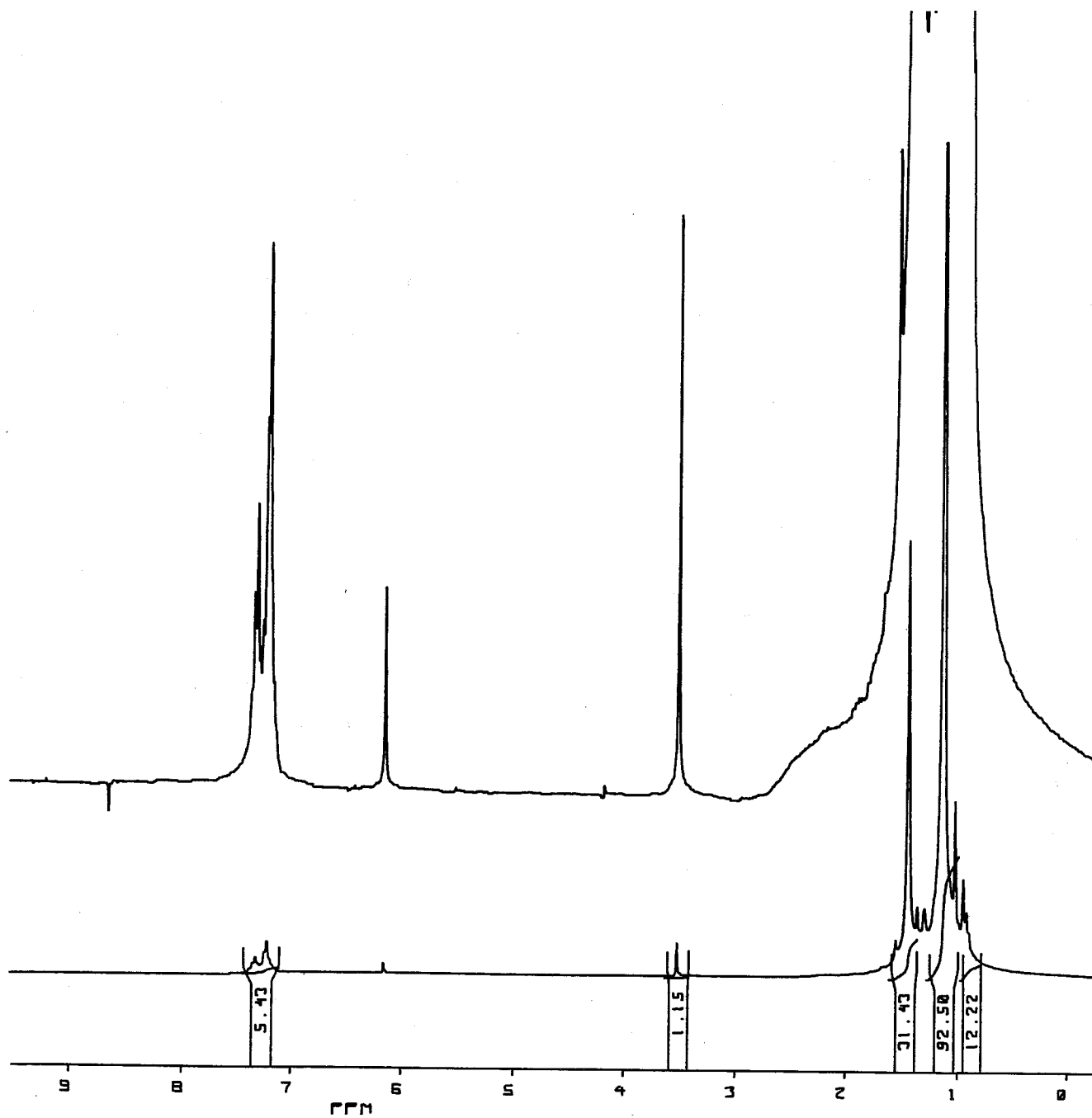


Figure 2: The ^1H NMR spectrum of PIB-DPE capped. The reaction was quenched with pure methanol

References:

1. Macromolecules, 19, 6, 1986, 1775-1777
2. First progress report (September-November 1992)