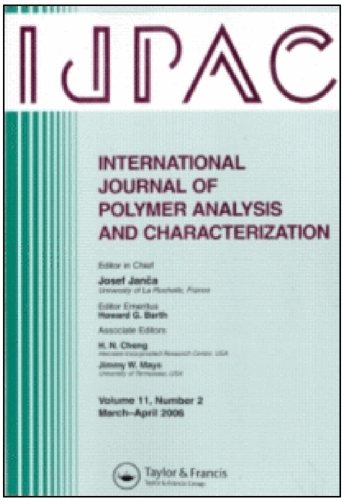

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Reaction of 1,1-Diphenylethylene with Lithium. Characterization and Stability of the Resultant Initiator

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1,1,4,4-Tetraphenyl-1,4-dilithiobutane (TPDLi) was prepared, by using high vacuum techniques, from 1,1-diphenylethylene and lithium metal, in tetrahydrofuran (THF)/benzene (4/1 by vol.) mixture, at room temperature and at 0°C. The quality of the difunctional initiator (DFI) was evaluated by polymerizing styrene and by characterizing the neutralized by (methanol) DFI, GC/MS and NMR spectroscopy. The TPDLi prepared at 0°C is almost 100% difunctional whereas the TPDLi prepared at room temperature is contaminated by the monofunctional species $LiCPh_2CH_2CH_2CPh_2(CH_2CH_2CH_2CH_2OLi)$ (~ 30%), produced from the reaction of one of its active centers with THF.

Keywords: 1,1-Diphenylethylene; Lithium; 1,1,4,4-Tetraphenyl-1,4-dilithiobutane; GC/MS; NMR

INTRODUCTION

The development of difunctional initiators (DFI) has been a continuing effort[1–4] since the discovery of anionic polymerization. By combining two active centers in the same molecule, multiblock[5,6] co- (ABA, ABABA, etc), ter- (CBABC, etc) and quaterpolymers (DCBABCD, etc.) can be synthesized in less steps than by using

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monofunctional initiators (MFI) (MFI: n steps, while DFI: $(n+1)/2$ steps). Additionally, polymers with cyclic structure[3,7–13] or complex architectures e.g. H- and super H-shaped[14–16] can be produced.

1,1,4,4-Tetraphenyl-1,4-dilithiobutane (TPDLi) is one of the most popular DFI,[2,17] especially in the case of polar monomers i.e. (meth)acrylates[5–7,17] or vinylpyridines.[11,12,18,19] The reactivity of the highly hindered active centers is too low to participate in deleterious side reactions during the polymerization.

By using TPDLi Hogen-Esch and Toreki[12] prepared cyclic homo- and block copolymers of 2-vinylpyridine with styrene.[11,12,18,20] The DFI was synthesized by reacting 1,1-diphenylethylene (DPE) with lithium metal at 25°C in tetrahydrofuran (THF) and then purified by recrystallization from THF/hexane (2/3 by vol.) mixture.[20,21] Fetters and Morton[2] and Reed and Urwin[22] prepared the TPDLi in a benzene/anisole mixture at room temperature. The seeding technique with isoprene was used to increase the solubility of the DFI in hydrocarbon solvents.

In a previous paper,[23] the synthesis of 3-miktoarm star terpolymers of styrene, isoprene and methyl methacrylate (SIM) was reported. The interesting three phase microdomain structures of these terpolymers will be discussed in forthcoming papers.[24,25] The chlorosilane linking chemistry, which is usually used for the incorporation of polydienic and polystyrenic branches, fails in the case of poly(meth)acrylic branches.[26] For the synthesis of the SIM star terpolymers two chlorines of trichloromethylsilane were replaced by polystyrene (PS) and polyisoprene (PI), the third was transformed to $SiC(Ph)_2CH_2CH_2C(Ph)_2^-Li^+$ by using TPDLi, followed by polymerization *in-situ* of the methyl methacrylate. The TPDLi synthesized, in THF at room temperature, was contaminated by ~30% of monofunctional species. The purpose of this paper is to detect the side reactions leading to the monofunctional species in order to avoid them and to evaluate the stability of the TPDLi.

EXPERIMENTAL SECTION

Synthesis

High vacuum techniques were used for the synthesis of 1,1,4,4-tetraphenyl-1,4-dilithiobutane. Benzene, THF, and DPE were purified according to well known procedures.[27] DPE was used as solution in benzene (0.1–0.2 M). The synthesis of TPDLi was carried out in a specially designed all-glass apparatus (Figure 1). The reactor was attached to the vacuum line, checked for pinholes and flame-dried. The appropriate amount of lithium metal was introduced in the apparatus from A, under argon atmosphere, by breaking the vacuum for a short time and then tube A was sealed-off. The apparatus was reattached to the vacuum line and pumped out for a few hours. About 4 ml of *n*-BuLi solution in hexane (~ 1.6 M) was introduced through septum (B) by a syringe, for purging of the reactor. Purified benzene, about 30 ml, was distilled into flask C. The reactor was removed from the vacuum line by sealing-off at D. The whole apparatus was then

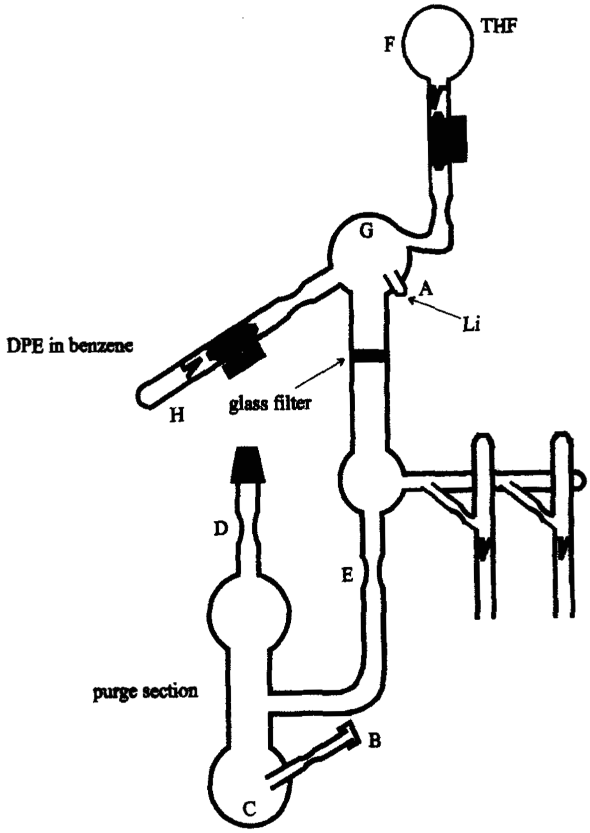


FIGURE 1 Apparatus for the synthesis of 1,1,4,4-tetraphenyl-1,4-dilithiobutane.

purged with the *n*-BuLi solution and rinsed by condensing vapors of benzene onto the walls. Finally the purge-section was removed by sealing-off at E. Two different experiments were performed.

In the first experiment (I), the synthesis of the initiator took place at 0°C (ice–water bath) for one day. THF (20–30 ml) was distilled from ampoule F containing THF and diphenylhexyllithium in flask G, which contained the Li excess (6-fold excess). When the distillation was completed the ampoule of THF was sealed-off. The solution of DPE (~ 1 mmol of DPE) in benzene (H) was added to THF and Li metal at 0°C under constant stirring. The final solution was THF/benzene, 4/1 by volume. The color of the solution changed from colorless to orange and finally to cherry red, which is the characteristic color of the initiator. The solution was left to react under stirring for one day at constant temperature (0°C) and then divided into ampoules. In the second experiment (II), the main variables that were changed were the temperature (room temperature) and the duration of the reaction (two days). Since there is THF in the reaction mixture in both cases, the solution was always thoroughly frozen with liquid nitrogen before sealing-off in order to avoid pyrolysis of the THF which could lead to termination reactions.[28] In both cases the concentration of the final solution was about 10^{-3} M.

Characterization of the Difunctional Initiator and Polymers Produced by It

The quality of the initiator prepared by the reaction conditions mentioned above was examined by three methods:

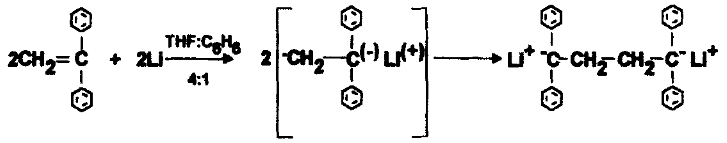
1. Polymerization of styrene in benzene at room temperature according to well established procedures.[27] The product was analyzed by size exclusion chromatography (SEC) at 30°C in THF using a Waters 510 pump, Waters 401 differential refractometer and four styragel columns with a continuous porosity from 10^6 to 10^3 Å.
2. A small portion of the initiator was neutralized with methanol and dried in the vacuum line. ^{1}H and ^{13}C NMR (Varian 540 Unity Plus) spectroscopy was performed in $CDCl_3$ at 35°C.
3. The neutralized initiator was dissolved in toluene (about 1%vol) and analyzed by gas chromatography/mass spectroscopy (GC/MS)

in a Hewlett-Packard model 5890 Gas Chromatograph connected to a Hewlett-Packard 5970 quadrupole Mass Spectrometer in electron impact ionization mode (EI–70 eV). Analytical conditions: Injection: cold on column, 0.5 µl solution in toluene. Column: HP5MS (crosslinked 5% methyl silicone) 30 cm × 0.25 mm.I.D., 0.25 µm thickness film (Hewlett-Packard). Carrier gas: Helium (64 KPa). The oven temperature was programmed from 100°C to 300°C at a rate of 10°C/min.

RESULTS AND DISCUSSION

The TPDLi was synthesized by reacting lithium metal with DPE. The radical anion first formed was dimerized immediately to yield the dianionic initiator according to Reaction 1.

The color of the reaction mixture changes almost immediately after the addition of DPE in the mixture of THF and Li metal. This indicates that this reaction is highly accelerated in the presence of polar solvents.[29] It was also observed that the Reaction1 is rather exothermic at the initial stages.



(1)

REACTION 1

As mentioned before the quality of the difunctional initiator was checked by polymerizing styrene in benzene at room temperature for one day. The deep red color of the initiator changed immediately to the orange of the polystyryllithium upon its addition to the styrene solution. The fast initiation step is due to the presence of THF which was used for the preparation of the initiator. The size exclusion chromatograms of the polystyrene prepared by the difunctional initiator synthesized at 0°C and at room temperature are given in Figure 2. In the case of the initiator prepared at room temperature the polymerization of styrene leads to two species with narrow molecular weight

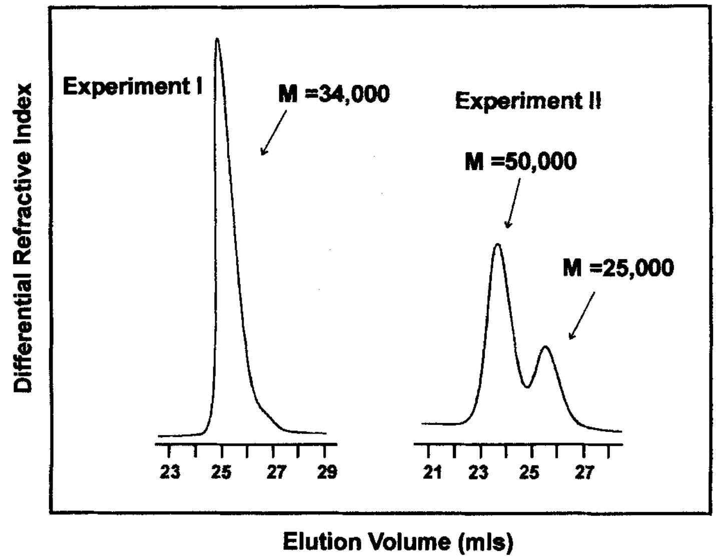
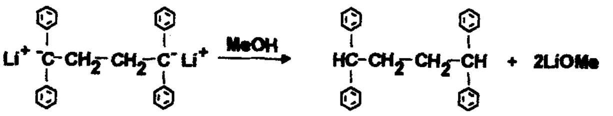


FIGURE 2 SEC chromatograms of polystyrenes produced by using the initiator produced from experiments I (THF at 0°C) and II (THF at room temperature).

distribution ($M_w/M_n < 1.1$, where M_w and M_n are, respectively, weight- and number-average molecular weight), one having double the molecular weight of the other. This indicates that the initiator is a mixture of monofunctional (MFI) and difunctional (DFI) species (approximately 3 : 7, respectively). However in the case of the initiator prepared at 0°C, the polymerization of styrene leads to the formation of one kind of species, almost exclusively, having very narrow molecular weight distribution ($M_w/\mathrm{M}_n < 1.1$). The molecular weight of the PS determined by SEC agrees very well with the one calculated from the relation:

$$M_n = \frac{\mathrm{gr_{styrene}}}{\mathrm{moles_{inhibitor}}} = \frac{5.0\ \mathrm{gr}}{1.5 \cdot 10^{-4}\ \mathrm{moles}} = 33{,}000.$$

The GC–MS chromatogram-spectrum of the methanol neutralized product of the experiment I are given in Figures 3 and 4. These figures prove that the neutralization product is almost 100% 1,1,4,4-tetraphenylbutane which is formed according to Reaction 2.^{1}H and ^{13}C NMR results (Figures 7 and 8) support this finding.



$$\mathrm{Li^{+}\,{}^{-}\overset{Ph}{\underset{Ph}{C}}{-}CH_2{-}CH_2{-}\overset{Ph}{\underset{Ph}{C}}{}^{-}\,Li^{+}} \xrightarrow{\mathrm{MeOH}} \mathrm{H\overset{Ph}{\underset{Ph}{C}}{-}CH_2{-}CH_2{-}\overset{Ph}{\underset{Ph}{C}}H + 2LiOMe} \qquad (2)$$

REACTION 2

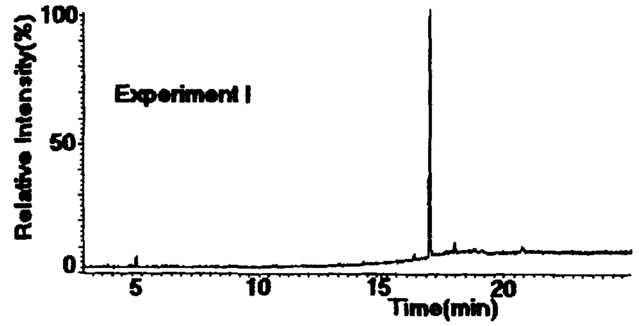


FIGURE 3 GC chromatogram of the neutralized with methanol product of experiment I (THF at 0°C).

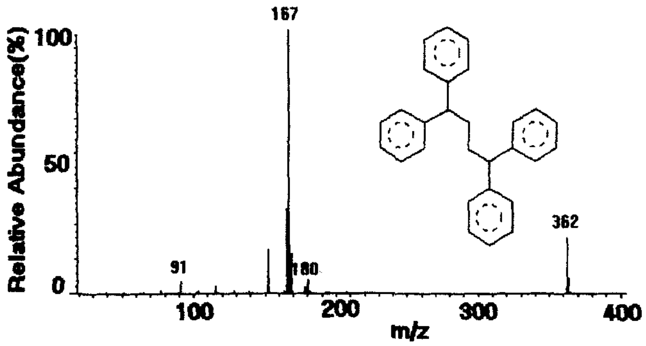


FIGURE 4 Mass spectrum of the main peak of Figure 3 and of the first main peak of Figure 5.

In the case of the neutralized with methanol product of the experiment II, the GC–MS chromatogram-spectra (Figures 5, 4 and 6) show the presence of a mixture of 1,1,4,4-tetraphenylbutane and $CH(Ph)_2CH_2CH_2C(Ph)_2C_4H_9O$, in a ratio 7 : 3 as calculated by the areas under the two peaks of the GC. From the ^1H and ^{13}C NMR spectra (Figures 9 and 10) one can conclude that the oxygen containing group is an alcohol and not an ether. The ratio of the DFI : MFI

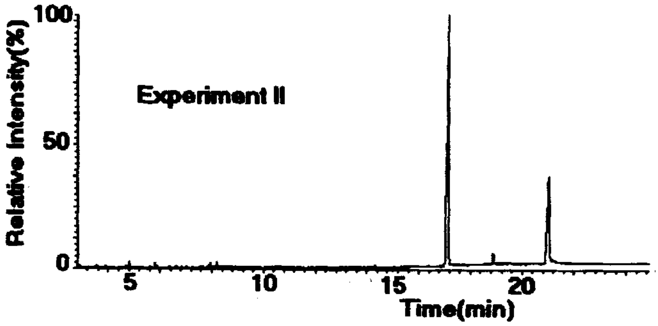


FIGURE 5 GC chromatogram of the neutralized with methanol product of experiment II (THF at room temperature).

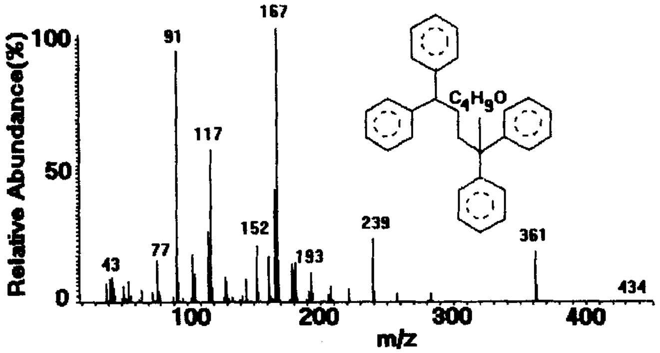
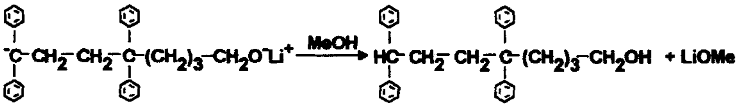


FIGURE 6 Mass spectrum of the second main peak of Figure 5.



$$Li^+\,{}^-C-CH_2-CH_2-C-(CH_2)_3-CH_2O^-Li^+ \xrightarrow{MeOH} HC-CH_2-CH_2-C-(CH_2)_3-CH_2OH + LiOMe$$ (3)

REACTION 3

was also calculated by the ^1H NMR peaks at 1.49 ppm (CH_2-e of Figure 9) and at 2.05 ppm (CH_2-b and b′ of Figure 9) and it was found equal to a ratio 6.8 : 3.2, in agreement with the results from SEC and GC/MS. It should be noticed here that $CDCl_3$ is not an hydrogen bond acceptor; consequently the chemical shift of the OH proton is greatly decreased and the OH peak occurs downfield from the CH_2 peak.[30] Consequently, the neutralization products are produced according to Reactions 2 and 3.

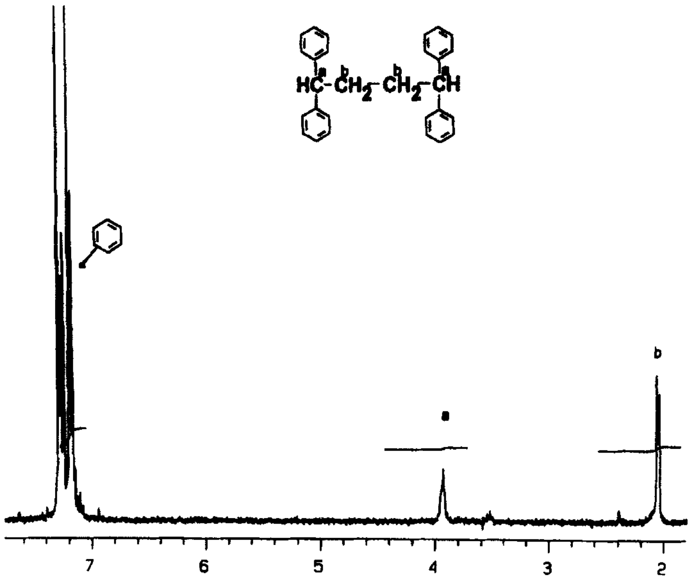


FIGURE 7 ^{1}H-NMR spectrum of the neutralized with methanol product of experiment I (THF at 0°C) recorded in CDCl$_3$.

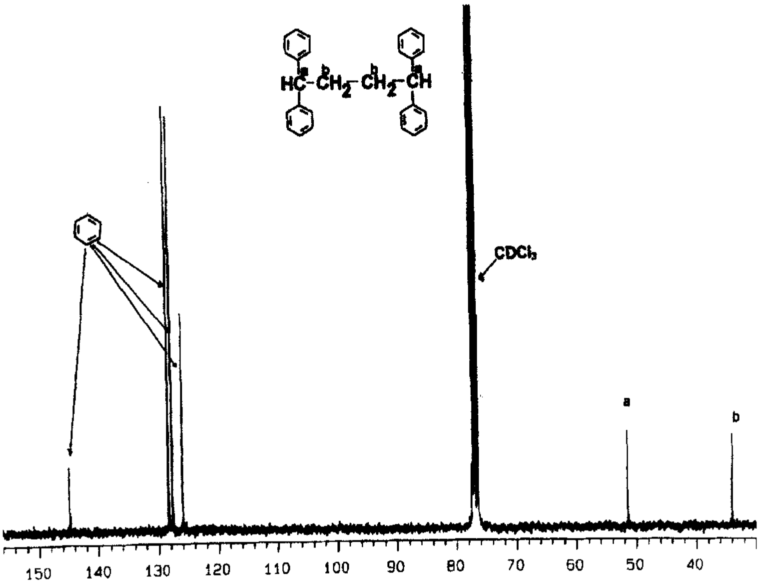


FIGURE 8 ^{13}C-NMR spectrum of the neutralized with methanol product of experiment I (THF at 0°C) recorded in CDCl$_3$.

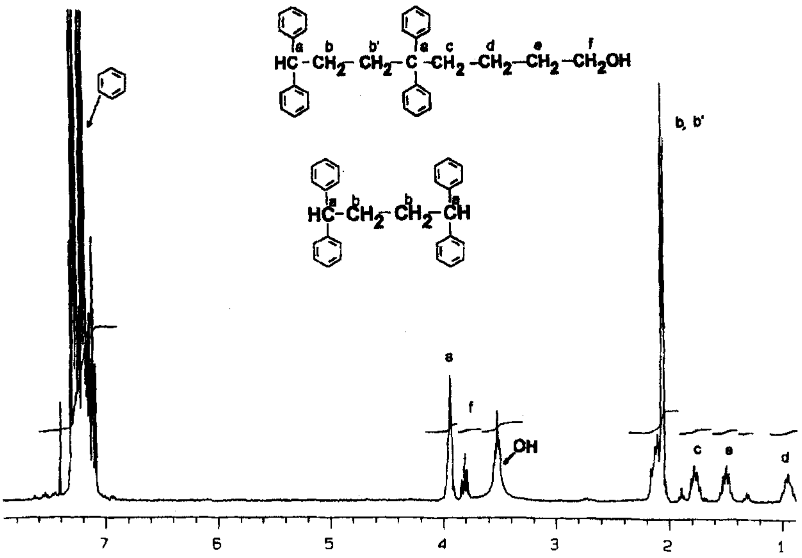


FIGURE 9 ^{1}H-NMR spectrum of the neutralized with methanol product of experiment II (THF at room temperature) recorded in $CDCl_3$.

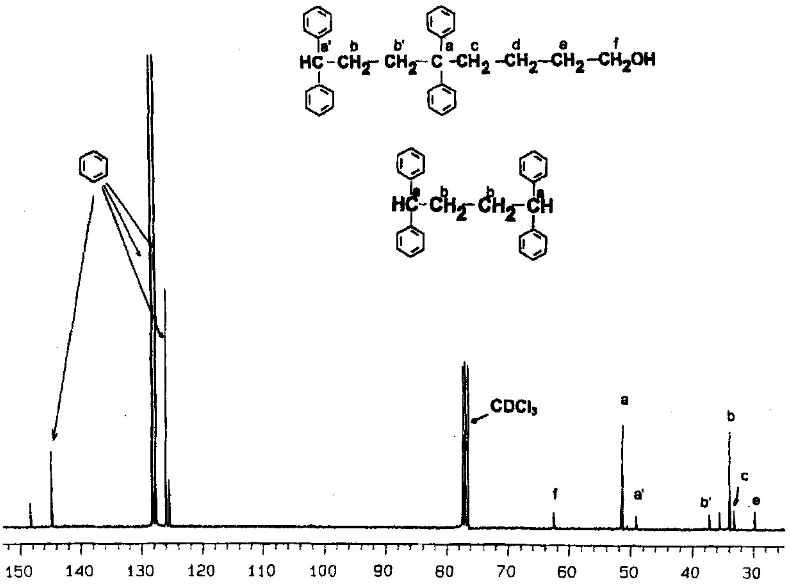
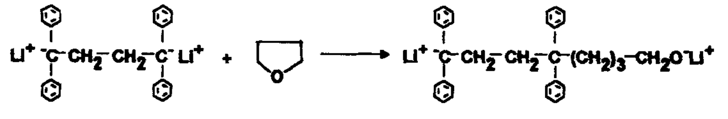


FIGURE 10 ^{13}C-NMR spectrum of the neutralized with methanol product of experiment II (THF at room temperature) recorded in $CDCl_3$.

This is rationalized by the fact that at relatively high temperatures organolithium compounds react with one molecule of THF[31] giving the lithium alkoxide compounds which are not capable to polymerize styrene. In our case the monofunctional species are produced according to Reaction 4.



(4)

REACTION 4

It was determined by SEC, GC–MS and NMR spectroscopy that pure DFI is stable at –20°C for at least one month, and that after six months about 10% monofunctional species are present.

In conclusion, almost 100% pure TPDLi can be synthesized in THF at 0°C and can be kept without reacting with the solvent THF at – 20°C for at least one month. At room temperature the difunctional initiator produced is contaminated with 30% of monofunctional initiator as proved by SEC, GC/MS and NMR spectroscopy.

Acknowledgments

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