Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthetic Applications of Nonpolymerizable Monomers in Living Cationic Polymerization: Functional Polyisobutylenes by End-Quenching

Savvas Hadjikyriacou[a]; Zsolt Fodor[a]; Rudolf Faust[a]
[a] College of Arts and Sciences University of Massachusetts Lowell One University Avenue, Lowell, Massachusetts

To cite this Article Hadjikyriacou, Savvas , Fodor, Zsolt and Faust, Rudolf(1995) 'Synthetic Applications of Nonpolymerizable Monomers in Living Cationic Polymerization: Functional Polyisobutylenes by End-Quenching', Journal of Macromolecular Science, Part A, 32: 6, 1137 — 1153

To link to this Article: DOI: 10.1080/10601329508011031

URL: http://dx.doi.org/10.1080/10601329508011031

J.M.S.—PURE APPL. CHEM., A32(6), pp. 1137–1153 (1995)

SYNTHETIC APPLICATIONS OF NONPOLYMERIZABLE MONOMERS IN LIVING CATIONIC POLYMERIZATION: FUNCTIONAL POLYISOBUTYLENES BY END-QUENCHING

SAVVAS HADJIKYRIACOU, ZSOLT FODOR,† and RUDOLF FAUST*

College of Arts and Sciences
University of Massachusetts Lowell
One University Avenue, Lowell, Massachusetts 01854

ABSTRACT

The chemistry and kinetics of 1,1-diphenylethylene (DPE) addition to living polyisobutylene was studied at −80°C in methyl chloride/*n*-hexanes or methylcyclohexane 40/60 v/v. Only monoaddition occurred even when large (9-fold) excess of 1,1-diphenylethylene was used. The kinetics of addition was established by ^{1}H-NMR spectroscopy and by conductivity measurements. The methanol-quenched polymer of the DPE-capped PIB carried exclusively $-OCH_3$ functionality, suggesting that all diphenyl alkyl chain-ends are ionized, which was confirmed by conductivity studies. It was determined that the diphenyl alkyl chain-ends are completely ionized when $[TiCl_4]/[\text{chain end}] \geq 2$ for chain-end concentrations $\geq 10^{-3}$ M. Close to quantitative end-quenching was achieved with 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene and 1-cyclohexenyloxy-trimethylsilane.

---

†Visiting scientist. Permanent address: Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17, Hungary.

INTRODUCTION

During the last decade advances have been made in living carbocationic polymerization toward the synthesis of well-defined materials with controlled molecular weight and molecular-weight distributions. The synthesis of block copolymers has also been accomplished by sequential monomer addition but only with monomers having similar reactivities. Thus the synthesis of polystyrene–polyisobutylene–polystyrene (PSt–PIB–PSt) triblock copolymer thermoplastic elastomer could be achieved [1], while the crossover efficiency was found to be low from the PIB living end to *p*-methylstyrene (pMeSt) [2], and even lower to α-methylstyrene (αMeSt) [3] or isobutyl vinyl ether [4], i.e., to more reactive monomers. Success also remains limited in the synthesis of functional polymers by in-situ functionalization of the living carbocationic chain ends. While the malonate anion [5], certain silyl enol ethers [6], and silyl ketene acetals [7] have been successfully used as functionalizing agents for vinyl ethers, only chloro- and allyl-functional PIBs have been reported [8]. The lack of success is due to the nature of living cationic polymerization. In contrast to living anionic polymerization, in living cationic polymerizations the concentration of active species, i.e., the cations, is often very small since most of the chain ends are in a dormant form. For instance, with the alkyl halide/BCl_3 or $TiCl_4$ initiating systems in the polymerization of isobutylene (IB) or styrene (St), the dormant form is the chloro-terminated species in equilibrium with the cations.

The equilibrium constant with a given initiating system depends on the stability of the polymer cation. For IB, St, or pMeSt the equilibrium constant is very

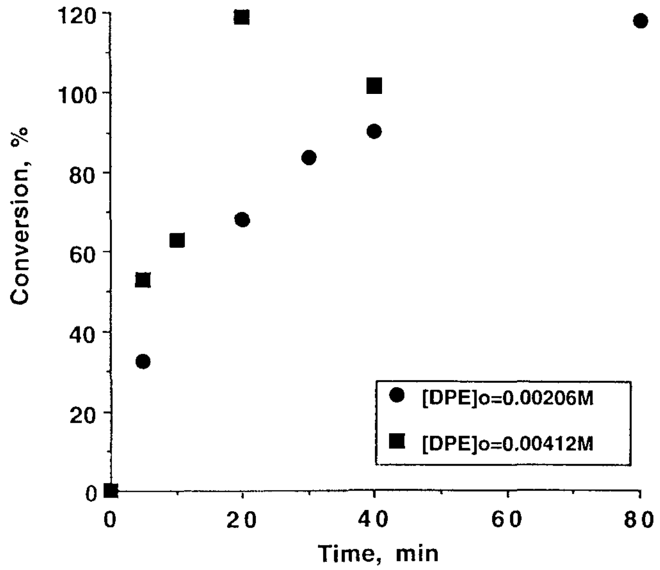


FIG. 1. The conversion of PIBCl (M_n = 2100, M_w/M_n = 1.20, conversion of IB ~ 100%, initiator efficiency = 93.6%) in the capping reaction at two different starting concentrations of DPE as a function of time. $[TiCl_4]$ = 0.0364 M, $[PIBCl]_0 = 1.87 \times 10^{-3}$ M, [DTBP] = 0.004 M, −80°C, solvent: MeCl/Hx 40/60 v/v.

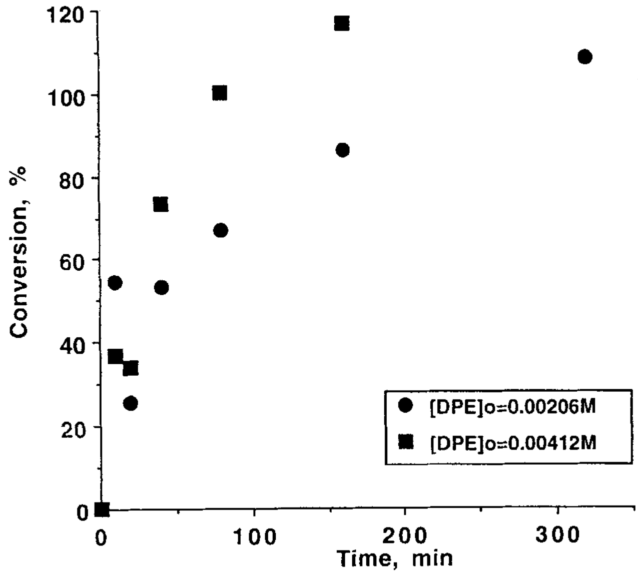


FIG. 2. The conversion of PIBCl (M_n = 2300, M_w/M_n = 1.27, conversion of IB ~ 100%, initiator efficiency = 88.5%) in the capping reaction at two different starting concentrations of DPE as a function of time. [$TiCl_4$] = 0.016 M, [PIBCl]$_0$ = 1.77 × 10^{-3} M, [DTBP] = 0.004 M, −80°C, solvent: MeCl/Hx 40/60 v/v.

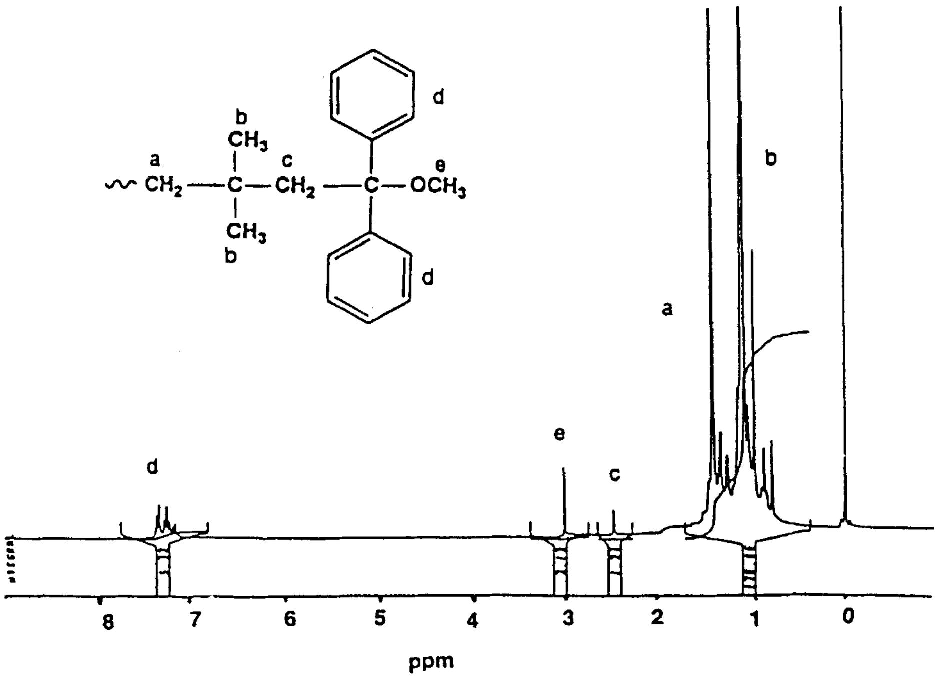


FIG. 3. The ^{1}H-NMR spectrum of the DPE-capped PIBCl. [DPE] = 1.25 × [PIBCl] in Hex/MeCl 60/40% v/v at −80°C.

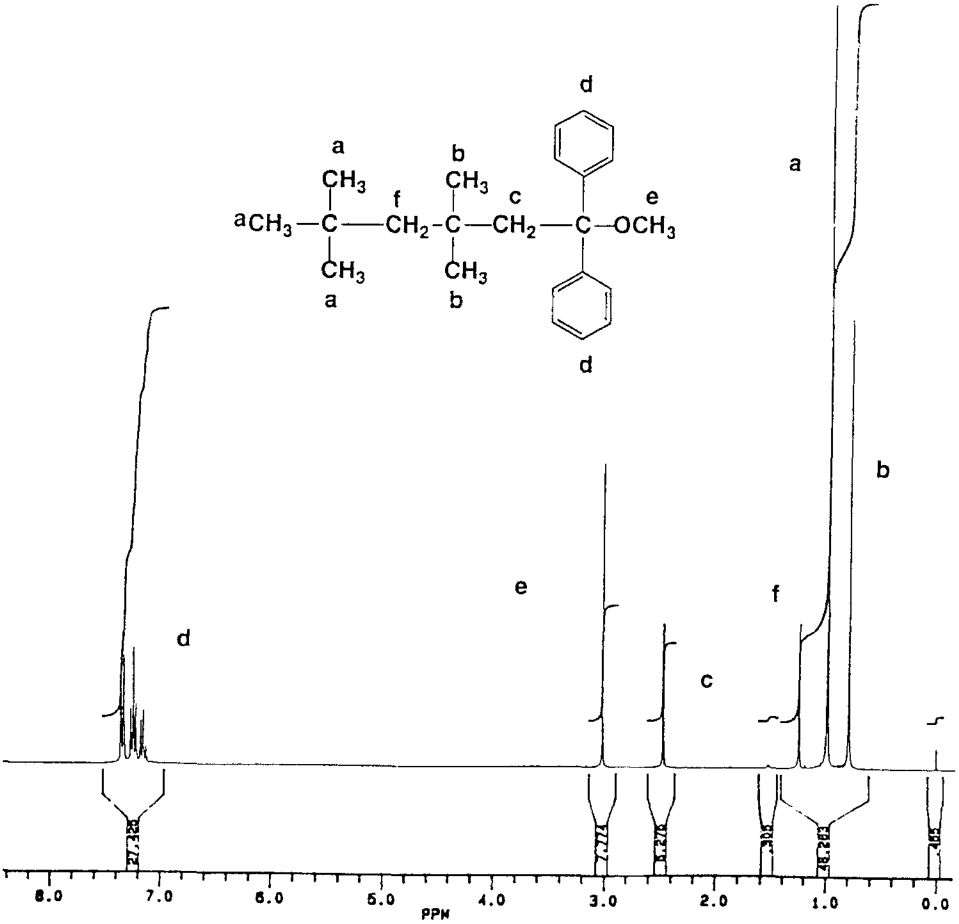


FIG. 4. The ^{1}H-NMR spectrum of the DPE-capped TMPCl. [DPE] = 1.25 × [TMPCl] in Hex/MeCl 60/40% v/v at −80°C.

small and therefore the addition of nucleophiles could not lead to the desired functional polymers [8, 9]. Quenching the polymerization of 2,4,6-trimethylstyrene with methanol yielded a mixture of chloro and methoxy ends [10], indicating the increased stability of the growing chain ends.

We have recently discovered that 1,1-diphenylethylene (DPE) adds to the PIB chain end quantitatively. The resulting diphenyl alkyl cation is an efficient initiating species for the polymerization of reactive monomers, hence the clean synthesis of block copolymers was predicted by first transforming the polymer chain ends to diphenyl alkyl cations by DPE capping. The success of the method was demonstrated by the clean synthesis of PIB-based diblock and triblock copolymers having PpMeSt or PαMeSt end segments [11-13]. Furthermore, functionalizations by a variety of nucleophiles may now be achieved.

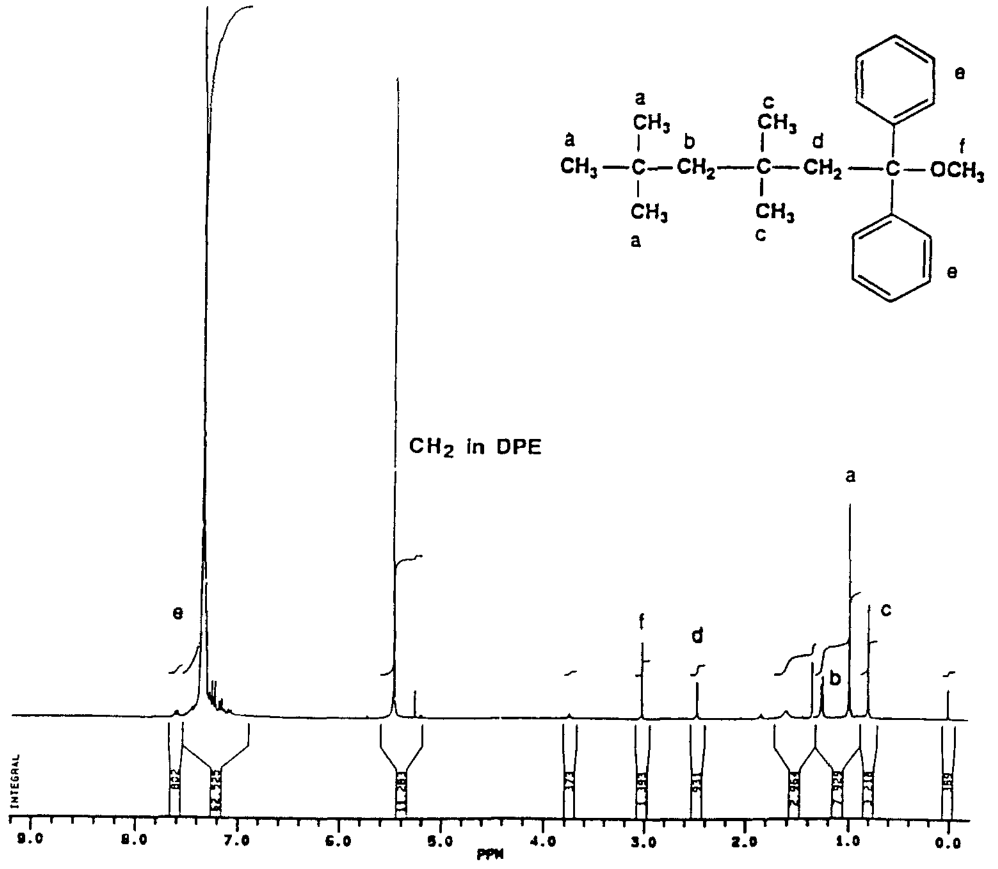


FIG. 5. The ^{1}H-NMR spectrum of the DPE-capped TMPCl ([DPE] = 10 × [TMPCl]). Peaks at 7.0–7.2 and 1.35 ppm are due to DTBP; traces of hexanes at 1.3 and 0.9 ppm.

A general methodology of using nonpolymerizable monomers as functionalization agents in living polymerizations was recently presented in an illuminating paper [14]. Specifically, the use of substituted DPE in anionic and of methyl 2-phenylpropenoate in group transfer polymerization was reported for the synthesis of functional polymers. It was also concluded that these concepts are general and applicable to any living polymerization. While this is feasible, as will become apparent later, synthetic application of nonpolymerizable monomers in living cationic polymerization is more universal. The present paper focuses on the chemistry and kinetics of DPE addition and the functionalization of the DPE-capped chain ends.

EXPERIMENTAL

Materials

DPE, phenyl magnesium bromide (3 M solution in diethyl ether), 1-methoxy-2-methyl-1-propenyloxy-trimethylsilane, 1-cyclohexenyloxy-trimethylsilane, and lith-

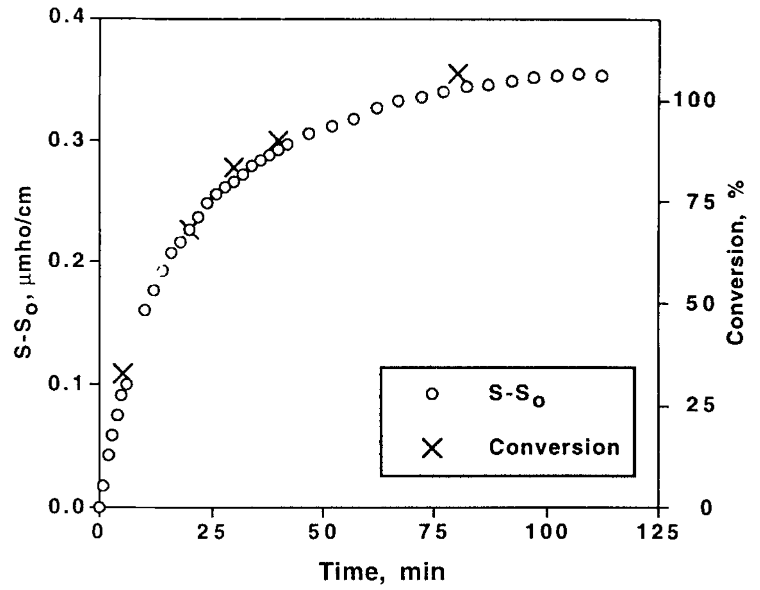


FIG. 6. The conversion of PIBCl and the corrected conductivity ($S - S_0$) of the reaction mixture in the capping reaction at $[DPE]_0 = 0.00206$ M as a function of time. Other details in the legend of Fig. 1. S_0 and S are the conductivities of the reaction mixture before and after DPE addition, $S_0 = 0.13$ µmho/cm.

ium diisopropyl amide (2 M solution in heptane/tetrahydrofuran/ethylbenzene) were used as received from Aldrich. 1,1-Diphenyl-3,3,5,5-tetramethyl hexyl-1-methyl ether (DTHOMe) was obtained by the reaction of 2-chloro-2,4,4-trimethylpentane (TMPCl) and DPE (25% molar excess over TMPCl) in the presence of $TiCl_4$ (fourfold excess over TMPCl) at −80°C in hexane (Hex)/methyl chloride (MeCl) 60/40 v/v followed by quenching with MeOH. 1-Chloro-1,1-diphenyl-2,2-dimethyl propane (DPDMPCl) was synthesized according to Reference 15. All other materials have been described [16].

Procedures

Capping Reactions

The polymerizations of IB were carried out as described [16]. When the IB conversion reached ~100%, DPE was introduced and allowed to react for a time predetermined by conductance measurements to be necessary to achieve complete capping. The reactions were quenched by the addition of prechilled methanol (MeOH) and the mixtures were poured into excess 10% ammonical MeOH. The polymers were purified by repeated dissolution and precipitation in hexanes/methanol and dried in vacuum prior to characterization.

Functionalizations

In order to ensure identical molecular weights for all functionalized PIBs, the polymerization of IB was carried out in a 1-L three-neck flask. After the capping

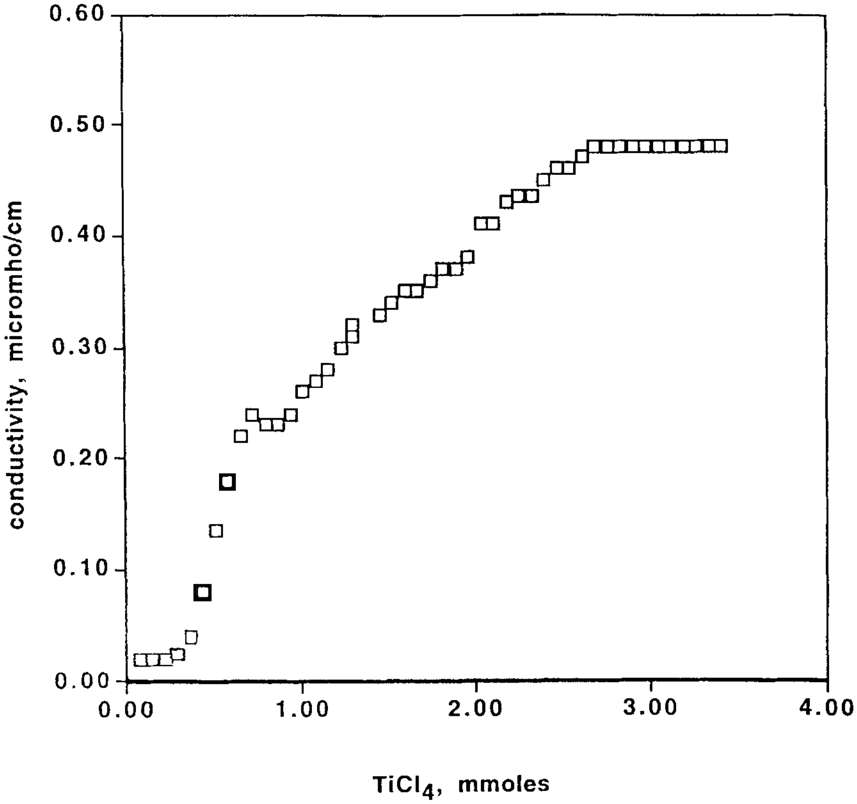


FIG. 7. Conductometric titration of DTHOMe (0.9 mmol) with $TiCl_4$ solution at −80°C.

reaction was over, 25 mL of the reaction mixture was delivered into culture tubes precooled to −80°C that were used for functionalization. The functionalizing agents were added and reacted for 2 hours, after which the reaction was quenched with prechilled MeOH and the contents were poured into excess 10% ammonical MeOH.

Conductivity measurements were carried out using a YSI Model 35 conductance meter equipped with a cell of 1 cm^{-1} cell constant and a BBC Goertz Metrawatt SE120 plotter.

Infrared spectroscopy was carried out by a Perkin-Elmer FT-IR Spectrophotometer 1760X. All other polymer characterizations have been described [16].

The calculations for the DPE content of the DPE-capped PIB was based on ^{1}H-NMR spectra using the CH_3 at 1.12 ppm (A_{CH3}), and CH_2 at 1.42 ppm (A_{CH2}) of PIB and the aromatic peaks in the 7.1 to 7.5 ppm range (A_{ar}). The conversion of PIBCl to diphenyl alkyl chain end was calculated using the following formulas:

$$\text{Conv1} = 0.6 \times (\text{DP}) \times A_{ar}/A_{CH3}$$

$$\text{Conv2} = 0.2 \times (\text{DP}) \times A_{ar}/A_{CH2}$$

where (DP) is the degree of polymerization of PIB determined experimentally by gel permeation chromatography [16]. The average of the two results was used.

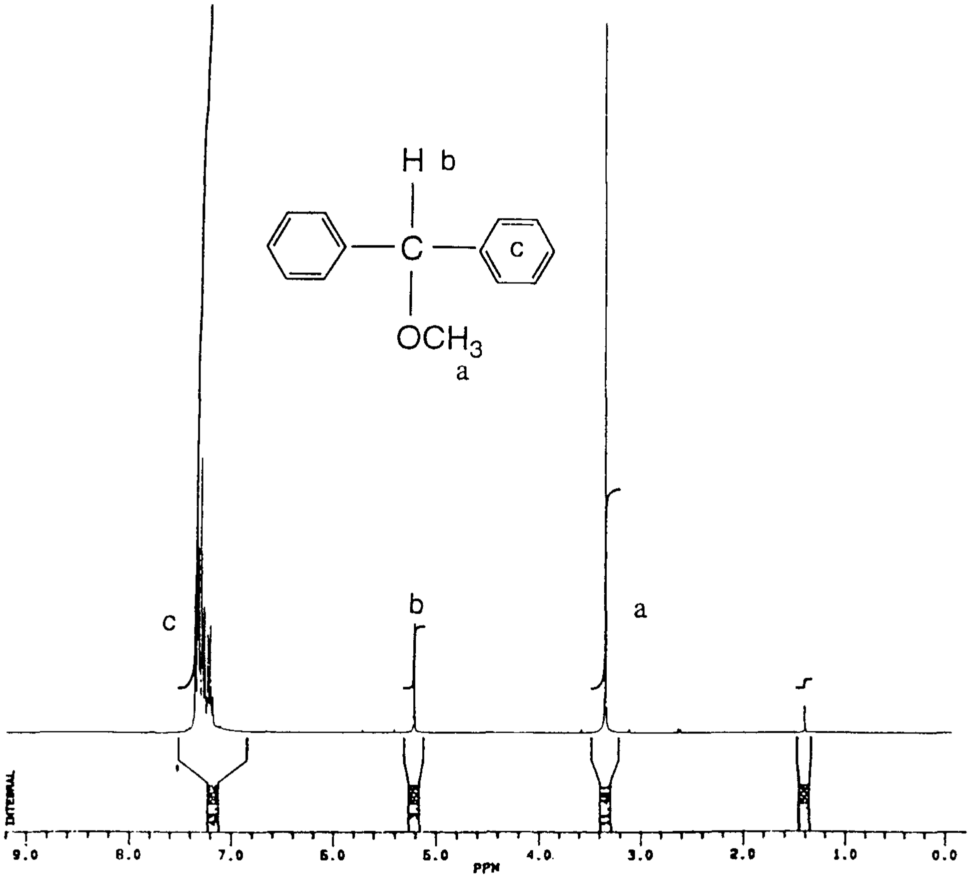


FIG. 8. The ^{1}H-NMR spectrum of the product after methanolysis of the chlorodiphenyl methane.

RESULTS AND DISCUSSION

Addition of DPE to the Living PIB End

The addition of DPE to anions or cations has been investigated by Evans et al. [17–20]. According to those results, monoaddition is strongly favored over diaddition. Only monoaddition occurred to butyl lithium (BuLi), even at [DPE]/[BuLi] = 1.8. A further reversible addition occurred with a large (6.3-fold) excess of DPE; however, the amount of diadduct was much less than the monoadduct, indicating that equilibrium lies well toward the monoadduct. DPE can form two types of diadducts in cationic addition, a linear diadduct (the linear dimer cation or 1,1,3,3-tetraphenyl but-1-ene formed by proton elimination from the dimer cation), and a cyclic diadduct (3-methyl-1,1,3-triphenyl indane formed by irreversible intramolecular alkylation). The kinetics of dimerization has been studied extensively [19, 23]. The initial rate of diadduct formation at [HCl] = 2.2×10^{-3} M, [$TiCl_4$] = 2.55

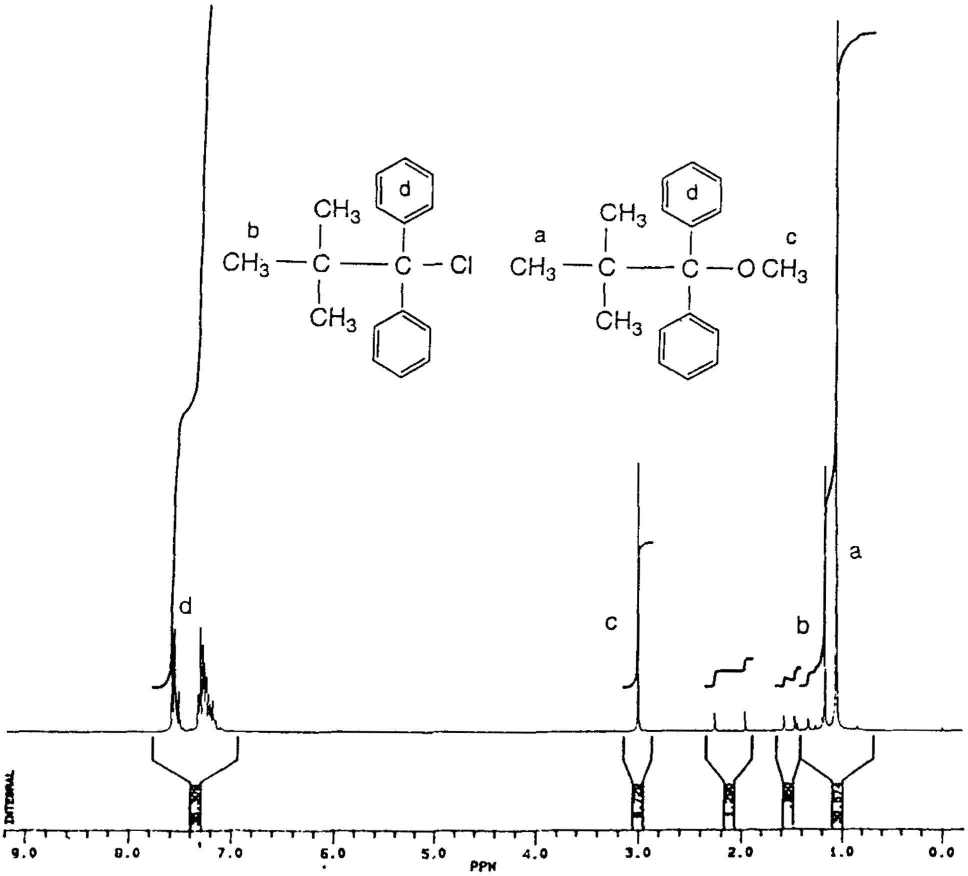


FIG. 9. The ^{1}H-NMR spectrum of the product after methanolysis of 1-chloro-1,1-diphenyl-2,2-dimethyl-propane.

× 10^{-2} M (very similar to our initiator-coinitiator concentrations), and [DPE] = 0.77 M in benzene at 55°C is 2.86 × 10^{-3} mol·L^{-1}·h^{-1}, i.e., the diadduct formation is very slow. More importantly, cyclic dimer formation was found to be even slower. Ortho-substituted DPEs do not dimerize due to steric hindrance [21]. The dimerization of DPE using protonic or Lewis acids was also investigated by Sigwalt et al. [22, 23]. With $TiCl_4$ in dichloromethane at −30°C, a rapid conversion of DPE to the indanic dimer was observed when using high DPE and $TiCl_4$ concentrations (~1 M) [23]. Similar to what was reported by Evans et al., it was concluded that the equilibrium between the monomeric and the dimeric cation lies toward the monomeric cation. Importantly, the cyclic dimer was not observed in the dimerization by $TiCl_4$ at −70°C [22].

Our initial experiments, carried out to determine the mode and kinetics of DPE addition to the living PIB chain end, were limited to −80°C using a MeCl/Hex or MeCl/methylcyclohexane (MeChx) 40/60 v/v solvent mixture. Two differ-

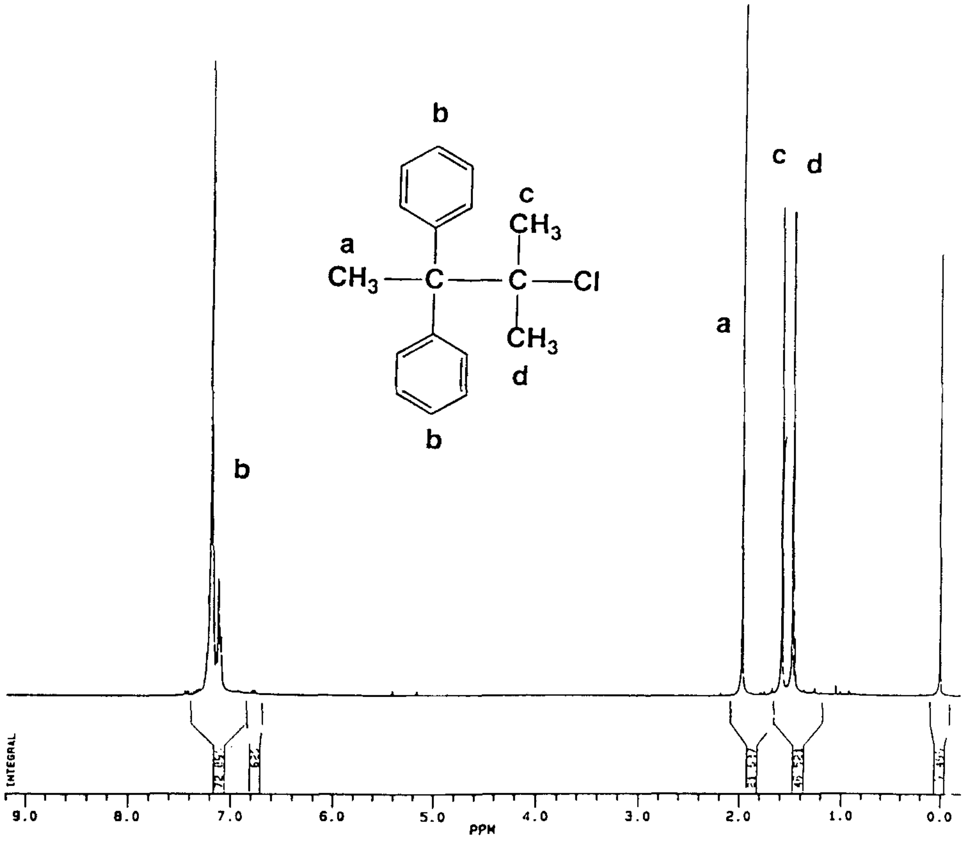
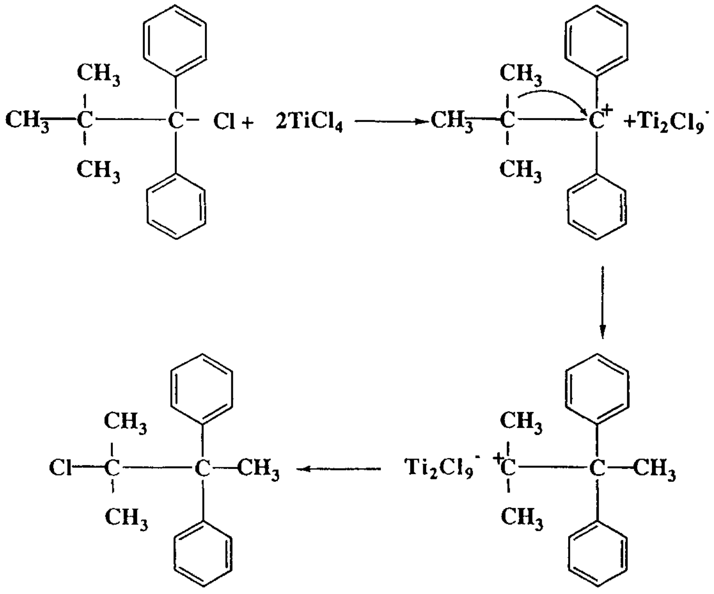


FIG. 10. The ^{1}H-NMR spectrum of the product after rearrangement on 1-chloro-1,1-diphenyl-2,2-dimethyl-propane.

ent $TiCl_4$ and DPE concentrations were studied. In Figs. 1 and 2 the conversion of the PIBCl chain ends to the corresponding diphenylalkyl chain ends is plotted against time for the MeCl/Hex solvent mixture. Similar plots were obtained with the MeCl/MeChx solvent mixture. The concentration of $TiCl_4$ strongly affects the reaction time required to reach complete capping. The ^{1}H-NMR of a reaction product of PIBCl ($M_n \approx 1500$) with DPE is shown in Fig. 3. Resonances due to the chloro end-group of PIBCl are absent, indicating complete capping. The assignments were confirmed by the ^{1}H-NMR spectrum of a model compound (Fig. 4) obtained by the capping of TMPCl using a small excess of DPE.

In Figs. 1 and 2, some conversions appear to be higher than 100% when $[DPE]_0/[PIBCl]_0 = 2$ was used. This may indicate more than one DPE units per PIB chain due to dimerization or copolymerization when DPE is added before the IB conversion is complete [13]. To determine the feasibility of diaddition, a reaction was carried out between TMPCl and DPE using a large excess of DPE $[DPE]_0 = 10 \times [TMPCl]_0$). The ^{1}H-NMR spectrum of the crude product is shown in Fig. 5.



SCHEME 1. Rearrangement of 1-chloro-1,1-diphenyl-2,2-dimethyl-propane.

The absence of peaks due to cyclic dimers (doublet between 3.2 and 3.4 ppm [23]) and the integration of the peaks reveal that only monoaddition occurred.

Since the diphenyl alkyl cation is colored, visible spectroscopy could be used to follow the reaction. Since an instrument equipped for low temperature was not available, conductivity measurements were used, in addition to NMR spectroscopy, to follow the capping reaction. Figure 6 shows the conductivity and the conversions (extent of capping) determined by ^{1}H-NMR spectroscopy. The two plots are similar, and the conductivity reaches its highest value at ~100% conversion. To verify that the chain ends were completely ionized, additional $TiCl_4$ was added, i.e., the concentration of the $TiCl_4$ was doubled after the DPE capping was complete. The conductivity did not increase, indicating that complete ionization has been reached. Diaryl alkyl chlorides are readily ionized in the presence of Lewis acids, for example, di-(*p*-methoxy-phenyl)-methyl chloride is completely ionized upon the addition of one equivalent of BCl_3 in dichloromethane [24]. Larger amounts of BCl_3 were required for complete ionization with para-CH_3 substituents and with para-CH_3 and $-$H, ionization was incomplete even in the presence of 200 equivalents of BCl_3.

To determine the necessary amount of $TiCl_4$ relative to the chain end to effect complete ionization, DTHOMe was titrated with $TiCl_4$ while the conductivity was monitored. DTHOMe was used in place of the chloride which is unstable at room temperature and undergoes elimination. The conductivity is plotted against the amount of added $TiCl_4$ in Fig. 7. Initially, $TiCl_4$ reacts with DTHOMe and converts

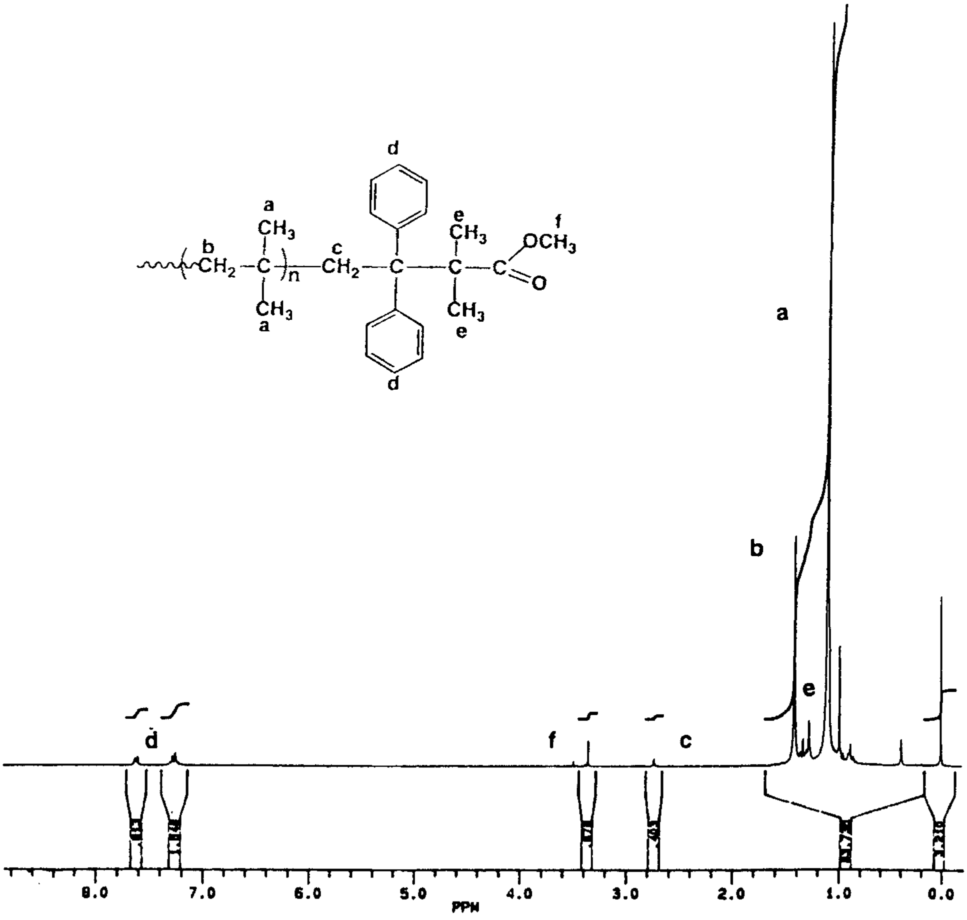


FIG. 11. The ^{1}H-NMR spectrum of the functionalization of polyisobutylene with 1-methoxy-2-methyl-1-propenyloxy-trimethylsilane.

it to the corresponding chloride (1,1-diphenyl-3,3,5,5-tetramethyl-1-chloro-hexane) (DTH-Cl). The conductivity of the system increases during this exchange due to the ability of $TiCl_3OMe$ to partially ionize the ends. Further addition of $TiCl_4$ increases the ionization of the chloride, and complete ionization is reached upon the addition of three equivalents of $TiCl_4$. We have reported that $TiCl_4$ forms bimolecular associates and/or bimolecular complex gegenions in the same solvent system at −80°C [16]. The fact that two equivalents of $TiCl_4$ are necessary for complete ionization of diphenyl alkyl chloride indicates that the gegenion is most probably $Ti_2Cl_9^-$.

Functionalization

According to ^{1}H-NMR spectroscopy, the MeOH-quenched polymer of DPE-capped PIB or TMPCl (Figs. 3 and 4) carries methoxy functionality exclusively, suggesting that all diphenyl alkyl chain-ends were ionized. This was confirmed by

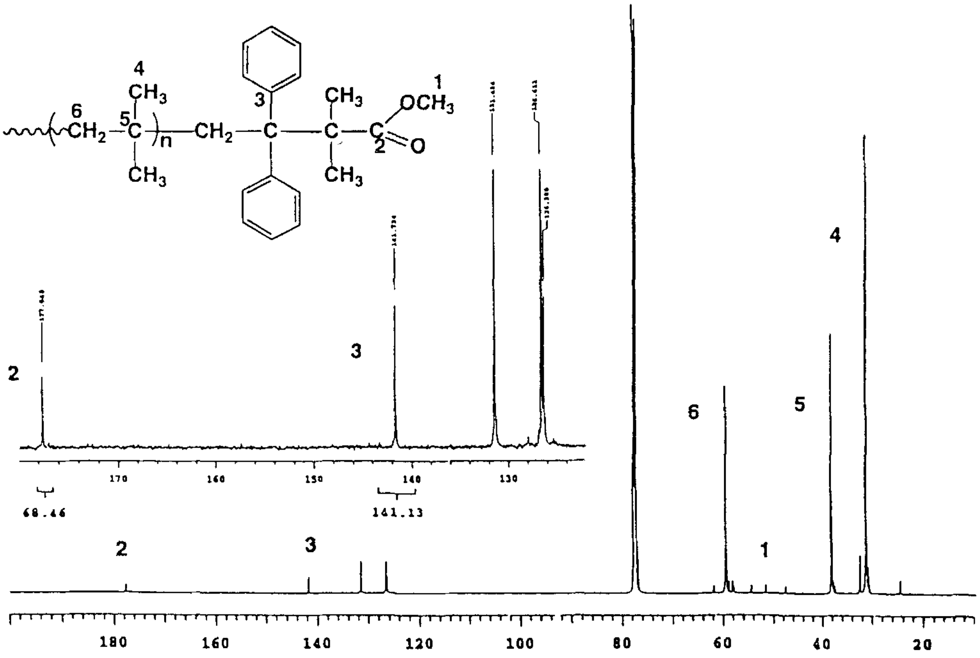


FIG. 12. Quantitative ^{13}C-NMR spectrum of the functionalization of polyisobutylene with 1-methoxy-2-methyl-1-propenyloxy-trimethylsilane.

conductivity studies. The methyl ether functionality is sensitive to acidic conditions and can be cleaved by weak acids. When methanol was used instead of ammonical methanol, unsaturation (6.13 ppm) always accompanied the —OMe functionality.

The presence of methoxy functionality alone is not a sufficient proof that the chain ends are completely ionized and that a direct reaction between the diphenyl carbenium ion and methanol will result. Solvolysis of the chloride may also explain the presence of methoxy functionality. It has been reported [25] that 1,1-diphenyl-1-chloroethane readily undergoes methanolysis in acetonitrile at room temperature with elimination as a competing reaction. Analysis of the kinetic deuterium isotope effects suggested that elimination and substitution proceed via a common carbocationic intermediate, most probably a contact ion pair type. We therefore decided to study the methanolysis of the model compounds diphenyl methyl chloride and DPDMPCl. The model compounds were dissolved in MeCl/Hex solvent mixture at −80°C. A proton trap (2,6-di-*tert*-butyl pyridine), 2 mL of prechilled MeOH, and 0.1 mL of $TiCl_4$ were subsequently added in this order. The reaction mixture was poured into ammonical MeOH, and the products were isolated, purified, and their ^{1}H-NMR spectra were recorded (Figs. 8 and 9). According to Fig. 8, diphenyl methyl chloride underwent complete nucleophilic substitution. Integration of the aromatic and methoxy protons (Fig. 9) indicates that only 64% of the DPDMPCl underwent nucleophilic substitution. A small amount of rearrangement was also observed. This rearrangement was studied in a separate experiment where $TiCl_4$ was added to a DPDMPCl solution in Hex/MeCl in the presence of a proton trap at

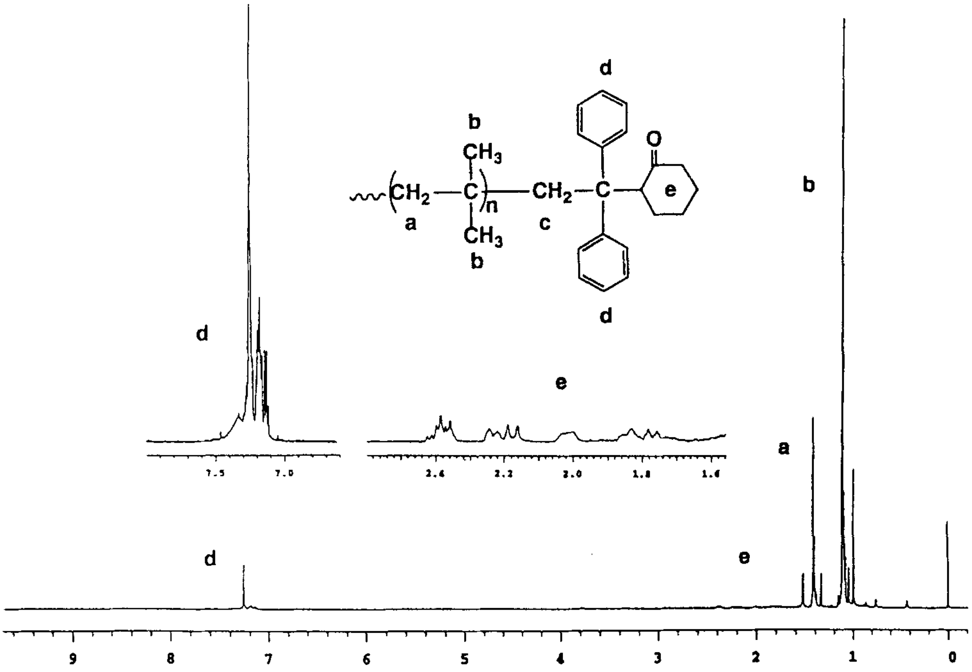


FIG. 13. The ^{1}H-NMR spectrum of the functionalization of polyisobutylene with 1-cyclohexenyloxy-trimethylsilane.

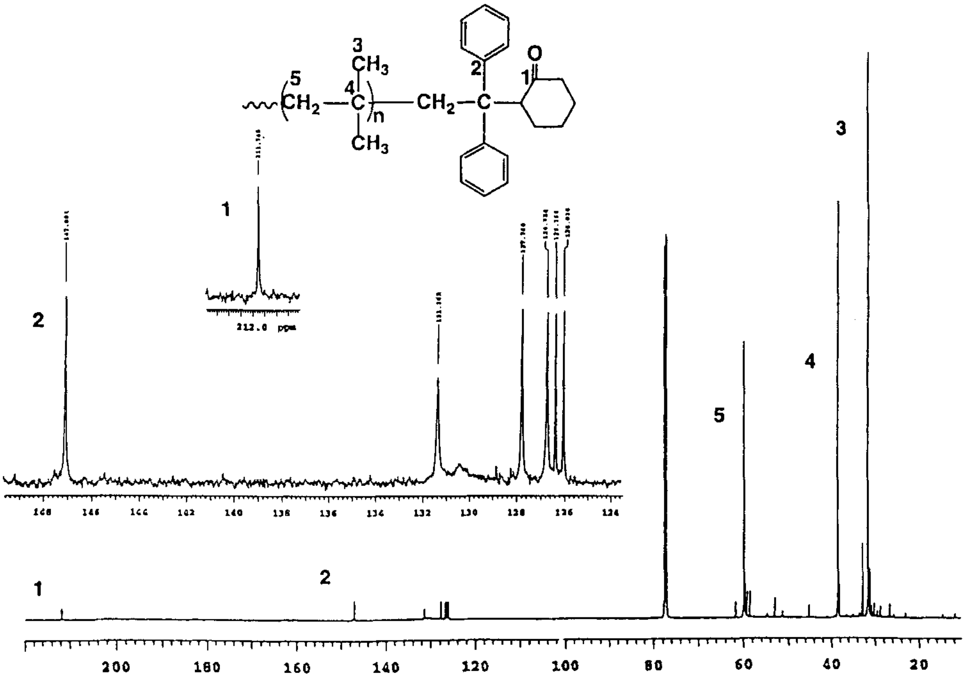


FIG. 14. Quantitative ^{13}C-NMR spectrum of the functionalization of polyisobutylene with 1-cyclohexenyloxy-trimethylsilane.

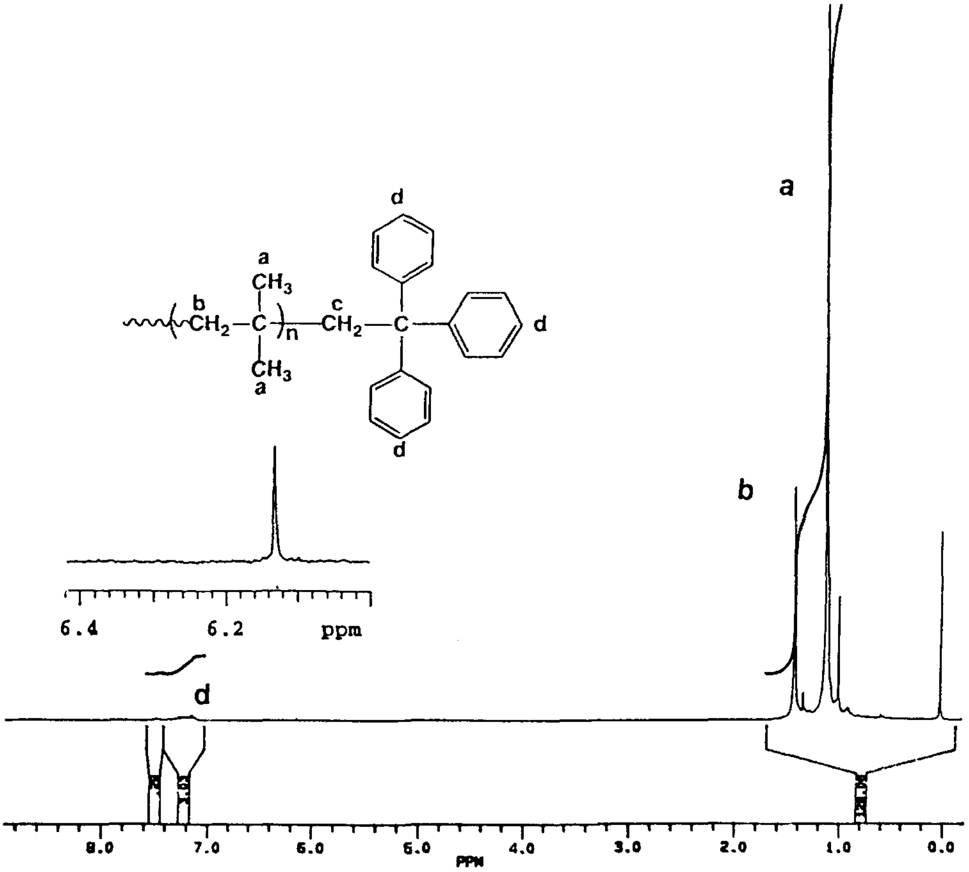


FIG. 15. The ^{1}H-NMR spectrum of the product of end quenching with phenyl magnesium bromide.

−80°C. After 1 hour the reaction was quenched with prechilled MeOH and the reaction mixture was poured into 10% ammonical MeOH. Upon purification, a white crystalline material was isolated. The ^{1}H-NMR spectrum, shown in Fig. 10, indicates that DPDMPCl underwent complete rearrangement. This is in agreement with the reported methyl group rearrangement that accompanies the dehydration of 1,1-diphenyl-2,2-dimethyl-1-propanol in the presence of acetic anhydride and acetyl chloride [26, 27]. The peak at 1.34 ppm (9H) of the original material disappeared and three other peaks appeared. The methyl group shifted to ~2 ppm (3H), while it appears that the two remaining methyl groups are no longer equivalent as they are separated at 1.55 ppm (3H) and 1.45 ppm (3H). The rearrangement is shown in Scheme 1. The original cation is sterically hindered as a trigonal coplanar structure, and a methide shift takes place in order to relieve the strain.

We conclude that the methoxy group at the chain end of the functionalized polymer is formed by the direct reaction between MeOH and the cation. Functionalization by other nucleophiles is also feasible. Close to quantitative functionalization (95%) was observed when the capping reaction was quenched with 1-methoxy-1-(trimethylsiloxy)-2-methyl-propene. The ^{1}H-NMR and the quantitative ^{13}C-NMR spectra of the ester functional PIB are shown in Figs. 11 and 12, respectively. Unsaturation (6.13 ppm) is negligible and the intensities of the corresponding peaks on both spectra are close to the theoretical values. The presence of the ester group at the chain end was also verified by FT-IR from the presence of a strong absorption at 1735 cm^{-1}. The ester functionality at the chain end provides a pathway for several classical reactions to acid, acyl halide, amide, enol, and hydroxy enol ethers [28].

Close to quantitative functionalization (95–97%) was also obtained when the capping reaction was quenched with 1-cyclohexenyloxy-trimethylsilane. The ^{1}H-NMR and the quantitative ^{13}C-NMR spectra of the ketone functional PIB are shown in Figs. 13 and 14. Unsaturation is absent, and the intensity of the corresponding peaks on both spectra are very close to the theoretical ones. The carbonyl presence was verified by a strong absorption at 1715 cm^{-1} in the FT-IR spectrum.

The ^{1}H-NMR spectrum of the product using phenyl magnesium bromide as quenching agent is shown in Fig. 15. About 20% of the product is olefin, most probably formed by proton elimination from the diphenylalkyl carbenium ion.

Other nucleophiles were also used for end-quenching. When lithium diisopropyl amide and sodium diethyl malonate were used, terminal olefin was the main product.

From the results it seems that steric hindrance may be a factor which should be considered when choosing nucleophiles for functionalization.

CONCLUSION

DPE, a nonpolymerizable monomer, was used to cap living PIB ends. Monoaddition is strongly favored over diaddition, and under the polymerization conditions, monoaddition occurs exclusively. Conductivity studies indicated that diphenyl alkyl chain ends are completely ionized. Thus, for the first time, a general route to functional polymers by end-quenching is feasible in the living carbocationic polymerization of olefins. Functional PIBs with close to theoretical functionality could be obtained by end-quenching using soft nucleophiles such as alcohols, silyl enol ethers, and silyl ketene acetals.

Research is continuing for the synthesis of functional polymers by in-situ functionalization of living carbocationic ends.

REFERENCES

[1] M. Györ, Zs. Fodor, H. C. Wang, and R. Faust, *Polym. Prepr.*, *34*(2), 562 (1993).

[2] Zs. Fodor and R. Faust, *J. Macromol. Sci.—Pure Appl. Chem.*, *A32*, 575 (1995).

[3] Y. Tsunogae and J. P. Kennedy, *J. Polym. Sci., Polym. Chem. Ed.*, *32*, 403–412 (1994).

[4] A. V. Lubnin and J. P. Kennedy, *Ibid.*, *31*, 2825 (1993).

[5] H. Shohi, M. Sawamoto, and T. Higashimura, *Macromolecules*, *25*, 58–63 (1992).

[6] H. Fukui, M. Sawamoto, and T. Higashimura, *Ibid., 26,* 7315 (1993).

[7] A. Verma, A. Nielsen, J. E. McGrath, and J. Riffle, *Polym. Bull., 23,* 563 (1990).

[8] B. Ivan and J. P. Kennedy, *J. Polym. Sci., Polym. Chem. Ed., 28,* 89-104 (1990).

[9] R. Faust and J. P. Kennedy, *Polym. Bull., 19,* 21, 29 (1988).

[10] R. Faust and J. P. Kennedy, *Ibid., 19,* 35 (1988).

[11] Zs. Fodor and R. Faust, *J. Macromol. Sci., A32*(12), 1985 (1994).

[12] Zs. Fodor and R. Faust, *Ibid., A32*(3), 575 (1994).

[13] D. Li and R. Faust, *Macromolecules, 28,* 43 (1995).

[14] R. P. Quirk and J. Ren, *Makromol. Chem., Macromol. Symp., 70-71,* 113 (1993).

[15] A. K. Zarkadis, W. P. Neuman, R. Marx, and W. Uzick, *Chem. Ber., 118,* 450 (1985).

[16] M. Györ, H. C. Wang, and R. Faust, *J. Macromol. Sci. – Pure Appl. Chem., A29,* 639 (1992).

[17] G. A. Evans, P. M. Jones, and J. H. Thomas, *J. Chem. Soc.*, pp. 104-111 (1957).

[18] G. A. Evans, P. M. Jones, and J. H. Thomas, *Ibid.*, pp. 2095-2104 (1957).

[19] G. A. Evans and E. D. Owen, *Ibid.*, pp. 4123-4125 (1959).

[20] G. A. Evans and D. Price, *Ibid.*, pp. 2982-2988 (1959).

[21] G. A. Evans, M. S. Peter, and J. H. Thomas, *Ibid.*, pp. 4563-4569 (1958).

[22] G. Sauvet, J. P. Vairon, and P. Sigwalt, *J. Polym. Sci., Polym. Chem. Ed., 16,* 3047-3064 (1978).

[23] G. Sauvet, J. P. Vairon, and P. Sigwalt, *J. Polym. Sci., Polym. Symp., 52,* 173-187 (1975).

[24] H. Mayr, R. Schneider, and S. Christian, *Makromol. Chem., Macromol. Symp., 13/14,* 4359 (1988).

[25] A. Thibblin and H. Sidhu, *J. Am. Chem. Soc., 114,* 7433 (1992).

[26] Mme. Ramart, *Compt. Rend., 173,* 1182 (1921).

[27] D. E. Bateman and C. S. Marvel, *J. Am. Chem. Soc., 49,* 2914 (1927).

[28] J. March, *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 3rd ed., Wiley, New York.

Received July 27, 1994
Revision received October 7, 1994